

THE CHEMISTRY OF PETROLEUM
AND ITS SUBSTITUTES

THE CHEMISTRY
OF
PETROLEUM AND ITS
SUBSTITUTES

A PRACTICAL HANDBOOK

BY

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WITH AN INTRODUCTION BY
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INTRODUCTION

By SIR BOVERTON REDWOOD, BART., D.Sc., F.I.C.

Past President Society of Chemical Industry; Adviser on Petroleum to the Admiralty, the Home Office, and the India Office

IT is impossible to read the excellent handbook on the Chemistry of Petroleum and its Substitutes, by Dr. C. K. Tinkler and Dr. F. Challenger, without being impressed with the scope which exists for the application of science in the treatment of petroleum.

The conversion of the raw material into the various commercial products is ordinarily effected by rule-of-thumb processes devised without adequate preliminary study of the chemical nature of the hydrocarbons dealt with, and without recognition of the scientific principles by which the manufacturer should be guided.

This has doubtless arisen from the abundance of the supply and the low cost of the raw material, from the facility with which products meeting the requirements of the consumer can be made, and in general from the manner in which the industry in petroleum has grown to its present vast dimensions.

It is obvious, however, that these conditions afford no justification for wasteful, unscientific methods of procedure, especially in view of the circumstance that as our stores of petroleum are being rapidly depleted we are doing an injustice to our descendants in utilizing these stores otherwise than economically and to the best advantage.

There is, happily, some evidence of increasing appreciation of the important help which science can afford in the refining of petroleum, and already there is a demand for highly-trained chemists in this branch of industry. Having regard to the large amount of British capital invested in petroleum enterprises, it is regrettable that it should be found necessary to seek abroad for men qualified for such positions.

The University of Birmingham was the first educational establishment to provide facilities for the systematic study

of the technology of petroleum, and it is appropriate that the first treatise on the chemistry of petroleum in its theoretical and practical aspects should have been written by the lecturers in chemistry at that university.

The authors have aimed primarily at providing a textbook for students who desire to become proficient in the chemical technology of petroleum, and they have admirably achieved their object by a skilful association of theory and practice. They properly consider that no man can become a successful technologist until he has fully mastered the underlying scientific principles of the subject. Hence a large but not disproportionate part of the present work is devoted to the pure chemistry of petroleum, and it is not until he has become fully acquainted with the fundamental principles, and has familiarized himself with the chemical and physical characters of the individual members of the various groups of hydrocarbons of which petroleum is composed, that the student is invited to study the practical applications of this knowledge. It will thus be seen that the book is much more than a mere aggregation of facts, for it is a highly commendable and successful attempt to bridge over the gap between the academic and the practical treatment of the subject with which it deals, and it should do much to pave the way to a better understanding of the intimate relation between pure and applied science, as well as of the extent to which the latter depends upon the former.

It remains to be added that whilst the work will be found of special value to the student it may be read with great advantage by all those whose avocations are directly or indirectly connected with the technology of petroleum, and even by that large section of the public whose interest has been aroused by a recognition of the extent to which petroleum has not only become one of the necessities of civilized life, but, as the motive power of submarines, destroyers, aeroplanes, dirigible balloons, armoured motor-cars, and army transport vehicles, has revolutionized the art of war.

PREFACE

THE increasing importance of petroleum as a source of various fuels both for internal and external combustion engines, together with the value of the lubricating oils which may be obtained therefrom, has of late years rendered extremely necessary the thorough scientific training of all those who are concerned with the isolation and distillation of the various petroleum products.

There is no doubt that for many years, especially before the introduction of the internal combustion engine, an enormous waste of the lower-boiling constituents took place. On the other hand, on the advent of the motor-car, these low-boiling fractions were eagerly sought after, and all but those with the very lowest specific gravity were discarded by the manufacturers of motor-spirit, although many of the intermediate fractions were eminently suitable for use in internal combustion engines.

It is to be hoped that in the future such matters will be in the hands of well-trained chemists, to whom the existence of a seemingly useless by-product does not immediately suggest a search for an easy method of getting rid of it, but rather the necessity of a painstaking investigation as to the possibilities of usefulness in other directions which may lie before it.

In common with a very few other educational institutions of a similar rank, the University of Birmingham has instituted a three years' course in petroleum mining, in which ample recognition has been made of the necessity for a thorough scientific training on the part of those who would become something more than mere rule-of-thumb prospectors.

The course at Birmingham, which was the first of its kind, was initiated by Professor Cadman, D.Sc., M.Inst.C.E.,

the Professor of Mining in the University of Birmingham, whose experience as Consulting Engineer to the Colony of Trinidad and Technical Adviser on Petroleum Mining to the Colonial Office, directed his attention to the necessity for such a course. The curriculum was designed in consultation with Sir Boverton Redwood. It extends over three years, and students taking the course are eligible to sit for the examinations for a Diploma, or for the Degree of B.Sc. in Mining.

As regards the chemical part of the course, in the first year the principles of inorganic chemistry are studied along with qualitative and volumetric analysis and elementary organic chemistry. The importance of this latter subject as an introduction to the more advanced and specialized work of the second and third years is sufficiently obvious.

The absence of a suitable book containing at the same time a certain amount of technological matter and the purely theoretical and practical organic chemistry necessary to a comprehension of the methods of the petroleum industry, has led us to the publication of this volume. It has arisen, we may add, out of manuscript notes originally intended solely for use by students working in the Birmingham University chemical laboratory.

The object we have had in view in planning the course has been, first of all, to familiarize the student with the methods of preparation of the various hydrocarbons and other substances used in connexion with them, and also with the manipulation of inflammable liquids.

Chapters on "cracking operations" and on the distillation of shale, coal, and wood, have been included, while special emphasis has been laid on the distillation of coal tar, since mixtures of benzene and toluene are already largely used in internal combustion engines.

In order that the principles involved in these commercial processes may be thoroughly understood, the carrying out of the methods on a small scale by each student forms an essential part of the course.

For the same reason we deal at some length with the question of alcohol and its modes of production and denaturing as well as the nature of the reactions underlying these

processes, since there is little doubt that the future will see large quantities of alcohol employed under conditions where we now use petrol.

We have included a short chapter on "saponifiable oils," and some of the methods employed in their analysis, since a certain amount of confusion may exist as to the points in which they differ from the so-called mineral oils, such as petroleum. Moreover, the adulteration of saponifiable oils with petroleum products is by no means unknown.

We have thought it advantageous to include a description of the methods of Sabatier and Senderens and of Paal and Skita for the catalytic hydrogenation of hydrocarbons and other substances.

The work of these chemists has attracted much attention in recent years, although among technologists there exists some misconception as to the application of their results.

We have attempted to indicate the close relations which exist between the various types of organic compounds, and to teach the reader how to infer the structure of a simple organic compound from its reactions, and conversely, reactions from a knowledge of constitution. We have chosen the practical exercises and arranged explanatory notes with this end in view, and have included a chapter on the characteristic properties, methods of formation and mutual interconversion of the more common classes of organic compounds. We have also introduced structural formulæ wherever possible.

As regards theoretical matter, we consider that a knowledge of the major portion of Chapter I is highly desirable for those who wish to approach in a broad-minded and scientific manner the manifold problems connected with the petroleum industry.

In general, Chapters II to XII deal more especially with petroleum products; Chapters XIII to XVII with benzene and its derivatives; and Chapters XVIII to XX with alcohol.

It is hoped that this volume will be found useful not only by those who are connected with the technology of petroleum, but that it will appeal to a wider circle, especially to those students to whom the application of the principles of pure

chemistry to technological processes appears attractive. We believe that much of the matter of this book has not been previously published in a collected form and within the scope of a single volume. This, we trust, may add to its usefulness.

Finally, we hope that this book will help to dispel from the mind of the student the idea which has up to the present been so fatal to the interests of British technology, namely, that there is a real difference between the so-called academic man of science and the technologist. In so far as the technologist fails to catch the spirit of research which characterizes the man of pure science, in so much does he fall short of his greatest possibilities.

The successful technologist must first of all be an academic scientist. In other countries this statement is regarded as a platitude, in England it is deemed by the majority visionary and unpractical.

We have much pleasure in expressing our sincere thanks to Professor Frankland, F.R.S., for many valuable suggestions which he has made from time to time.

It is perhaps hardly necessary to say that in arranging the subject-matter of this book, we have made frequent reference to Sir Boverton Redwood's "Treatise on Petroleum." We have also adapted (by permission of Messrs. C. Griffin & Co., Ltd.) certain descriptions of apparatus from J. A. Hicks' "Mineral Oil Testing." Other standard works which we have consulted are referred to in the text.

We gladly acknowledge the assistance we have received from Mr. F. H. Garner, B.Sc., who has kindly assisted us in the reading of the proofs.

Mr. Garner has also worked out some of the numerical examples in Chapter XXV. We are also much indebted to the following firms for the use of blocks for illustrations, Messrs. Baird & Tatlock (London), Ltd., Messrs. Standley Belcher & Mason, Ltd., and Messrs. Mansfield & Son, Ltd.

C. K. T.

F. C.

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THE CHEMISTRY OF PETROLEUM AND ITS SUBSTITUTES

CHAPTER I

INTRODUCTORY THEORETICAL MATTER

IN this chapter a brief summary will be given of the properties exhibited by the more important classes of carbon compounds. The methods of formation of typical members of each class will also be described.

It is hoped that the reader will keep the important truth always in view, that, in the study of organic chemistry whether pure or applied, it is not so much the remembering of the properties of various seemingly unrelated compounds, which is important, but, rather, an intelligent grasp of the general reactions to be expected from all the members of each group of compounds.

It is of little value to the student to know that aniline gives phenol when treated with nitrous acid, or that benzoic acid yields benzene on dry distillation with lime, unless he is immediately able to infer that xylydine will produce xylenol, and toluic acid toluene under similar conditions.

The student, when he learns the reactions of a substance which is new to him, should immediately ask himself, "Is this behaviour peculiar to this compound, or is it shared by other substances?" And if so, "To what circumstance is the similarity in properties to be attributed?"

In this direction lies progress and an intelligent grasp of what, when approached in any other way, will prove only a bewildering mass of seemingly meaningless transformations.

In order that satisfactory progress may be made in the theoretical principles of organic chemistry, it is essential that the student should thoroughly understand the conception of valency—at least, in its simplest form—and, moreover, that

he should do so almost at the commencement of the first year's course in Inorganic Chemistry.

The valency of an element may be expressed as being numerically equal to the number of atoms of hydrogen (or of another element, one atom of which combines with one atom of hydrogen) with which one atom of the element in question will combine. Similarly, the valency of an element is numerically equal to twice the number of atoms of oxygen (or of some other element, one atom of which combines with one atom of oxygen) with which one atom of the element will combine.

A determination of the composition of several of the simplest carbon compounds has shown us that in almost every case one atom of carbon combines with four atoms of a univalent, two of a divalent, and one of a quadrivalent element. Thus we have—

CH_4	CCl_4	CF_4	
Methane or marsh gas.	Carbon tetrachloride.	Carbon tetrafluoride.	
CO_2	COS	CSTe	CS_2
Carbon dioxide.	Carbon oxysulphide.	Carbon thiotelluride.	Carbon disulphide.
CSi	CZr		
Silicon carbide (carborundum).	Zirconium carbide.		

One single notable exception to this rule will readily occur to every student, though he may find it difficult to recall a second.

The molecule of carbon monoxide consists of a single oxygen atom linked to a single carbon atom. Either carbon is divalent in carbon monoxide or oxygen is quadrivalent.

Certain other substances exist of which the properties and composition may be explained on the assumption of the divalency of carbon; but their number is very small in comparison with the number of those compounds in which carbon is known to be quadrivalent.

Moreover, it is highly probable that the oxygen atom of certain organic compounds is quadrivalent, although a discussion of the evidence falls outside the scope of this book.

The doctrine of the quadrivalence of the carbon atom is therefore still accepted as the structural basis of the whole of organic chemistry.

We may now turn to a consideration of the various types of carbon compounds.

The term "hydrocarbon" is used to denote all those compounds containing exclusively carbon and hydrogen, and is to be distinguished carefully from the term "carbohydrate," which is applied to an entirely different class of compounds.

Hydrocarbons are classified into two main divisions: those which may be regarded as derivatives of methane, CH_4 , and those of which the parent substance is benzene, C_6H_6 . Indeed, almost all known organic compounds may be looked upon as derivatives either of methane or benzene.

Since the majority of the naturally occurring fats are found to be more or less directly related to methane, all derivatives of this hydrocarbon are known as fatty, or more usually, aliphatic compounds. The molecules of all these hydrocarbons consist of carbon atoms arranged in open chains.

On the other hand, those compounds in which the molecules contain carbon atoms arranged in a closed ring are designated Cyclic Compounds.

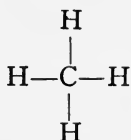
Those cyclic compounds having structures most closely resembling that of benzene are known as aromatic substances, since many benzene derivatives possess characteristic aromatic odours, and occur in extracts prepared from fruits and flowers.

OPEN CHAIN COMPOUNDS.

As mentioned above, the simplest aliphatic hydrocarbon is methane, or marsh gas. This colourless, inflammable gas is formed in marshes, owing to the action of bacteria on the plant residues embedded there.

It occurs in enormous quantities in coal mines, and is a constituent of the "natural gas" arising from petroleum wells in various parts of the world.

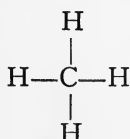
Its formula is represented thus—



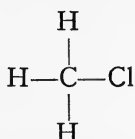
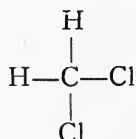
The bonds between the carbon atom and the four hydrogen atoms are convenient devices for expressing graphically that some definite force exists which binds four—and never more than four—hydrogen atoms to one atom of carbon.

If chlorine be mixed with methane and the mixture kept

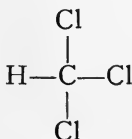
in diffused sunlight, the hydrogen atoms are gradually replaced by chlorine, and four different compounds are formed. At the same time hydrogen chloride is produced.



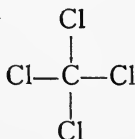
Methane.

Monochloromethane
(methyl chloride).

Dichloromethane.

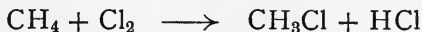


Trichloromethane (chloroform).



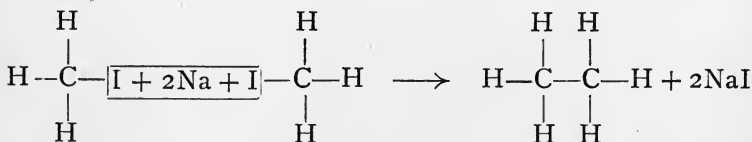
Tetrachloromethane.

The equations representing the other changes can readily be inferred if the first be given.



The replacement of the hydrogen atom by chlorine, with formation of hydrogen chloride, is an example of what is known as "substitution."* The hydrogen atoms of methane are said, therefore, to be capable of successive substitution by chlorine. Similarly, the hydrogen atoms of various other organic compounds can be substituted by bromine, fluorine, the nitro-group ($-\text{NO}_2$), the sulpho-group ($-\text{SO}_2 \cdot \text{OH}$), and so on.

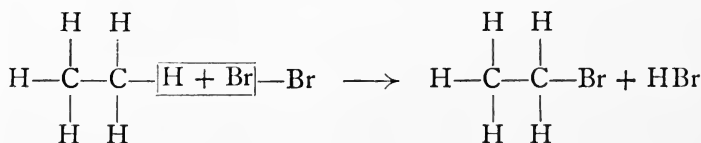
Now, if we take the gaseous compound monochloromethane, CH_3Cl , or rather, as being more convenient, the compound monoiodomethane, CH_3I , which is a liquid, and heat it with sodium, we obtain sodium chloride (or iodide) and a new gaseous hydrocarbon known as ethane, the properties of which are very similar to those of methane; its composition has been found to be represented by the formula C_2H_6 .



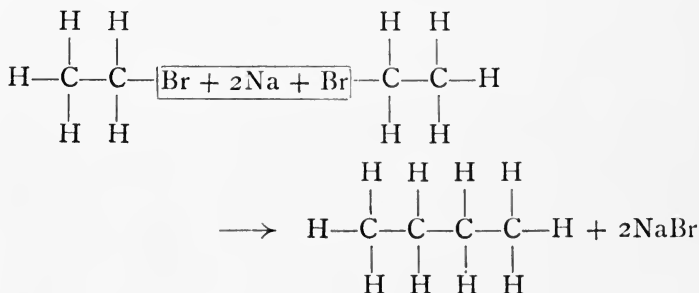
* This process of substitution by a halogen must carefully be distinguished from the totally different type of reaction known as "addition of halogen." In the latter case no halogen hydride is formed (see page 13).

This reaction is typical of many similar ones, and was discovered by Wurtz.

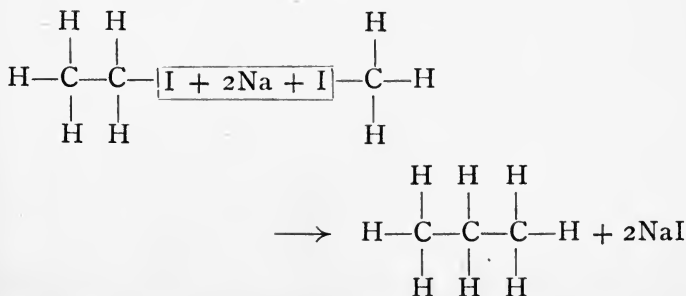
By the action of bromine on ethane a hydrogen atom can be substituted and eliminated as hydrogen bromide, thus—



The new compound is a liquid known as ethyl bromide, and can also undergo the Wurtz reaction with sodium, producing sodium bromide and a hydrocarbon C_4H_{10} , known as butane; its constitution has been found to be represented by the subjoined formula—

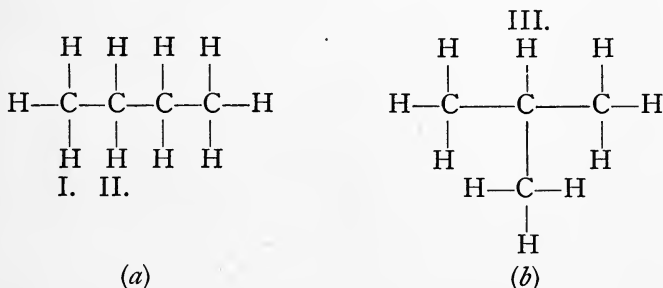


We have, therefore, so far, met with three aliphatic hydrocarbons: methane CH_4 , ethane C_2H_6 , and butane C_4H_{10} . Propane C_3H_8 , is produced by the action of sodium on a mixture of monoiodoethane and monoiodomethane, a method of formation which proves its constitution—



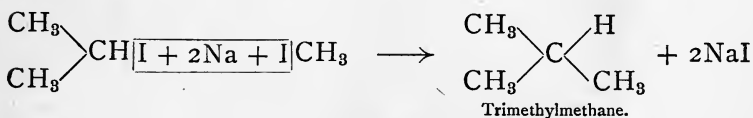
If it be attempted, whilst adhering to the doctrine of the

quadrivalency of carbon, to construct graphic formulæ for methane, ethane, and propane, other than those just given, it will be found impossible. On the other hand, the hydrocarbon C_4H_{10} may be written with a different arrangement of the atoms from that given above. Both the formulæ, for only two will be found possible, are given below—



In compound (a) the carbon atom marked I is designated a primary carbon atom, since it is linked to only one atom of carbon; that marked II, however, is a secondary carbon atom, since it is connected with two atoms of that element. By analogous reasoning, atom III in compound (b) is called a tertiary carbon atom.

A compound with a constitution represented by formula (b) could be prepared by the action of sodium on a mixture of isopropyl iodide (see page 7) and iodomethane (methyl iodide).



This substance, although possessing the formula C_4H_{10} , is found to be different in properties from the hydrocarbon C_4H_{10} obtained from ethyl bromide by the Wurtz reaction.

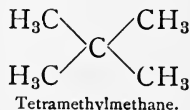
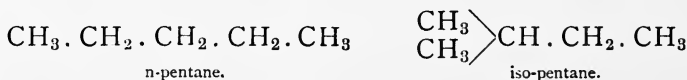
The difference in properties can be ascribed solely to the difference in the arrangement of the atoms within the molecule, a difference which finds expression in the formulæ.

Such substances possessing the same chemical composition, but a different constitution, are said to be *isomeric*, and are spoken of as isomers.

It will be noticed that in (a) there is a straight chain of carbon atoms. Such an arrangement is called a normal chain, and the particular substance in question normal

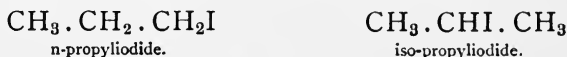
butane, usually written *n*-butane. In (*b*), however, the chain of atoms is branched and the hydrocarbon is known as iso-butane.

As the length of the carbon chain increases, the number of isomers increases rapidly. Pentane C_5H_{12} exists in three isomeric forms—



The hydrocarbon $C_{13}H_{28}$ should be capable of existing in 802 different isomeric forms, most of which have not yet been prepared, since more important problems are yet awaiting the attention of chemists.

The cases of isomerism among the pentanes and butanes and their derivatives are examples of what is known as structural isomerism. Thus two isomeric iodo-propanes are known represented respectively by the formulæ—



If we now make a list of the aliphatic hydrocarbons we have so far dealt with and place their formulæ alongside, certain facts will immediately be obvious—

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}

(i) Each member of the five differs from the preceding one in that its molecule contains one atom of carbon and two atoms of hydrogen more; in short, the difference between any two members of the series is to be represented by $n \times CH_2$.

(ii) The names of the hydrocarbons all end in -ane. This is intentional, and serves to indicate what has already been mentioned, viz. that they possess many properties in common.

(iii) The general formula for the series is C_nH_{2n+2} .

Later on we shall meet with many instances of series of

organic compounds, the members of which differ in composition from one another by $n \times \text{CH}_2$, and also possess many similar properties. Such series are called Homologous Series, and the various members Homologues. Thus ethane and pentane are higher homologues of methane.

The members of the homologous series of which methane is the first representative are known as Paraffins; several of the higher homologues occur in paraffin oil, paraffin wax, etc. The term is derived from the Latin *parum*, little, *affinis*, affinity, indicating the relative stability of these substances in presence of many powerful reagents.

Sulphuric, hydrochloric, chromic and nitric acids, potassium permanganate and dichromate, as well as alkalis, are without action on the paraffin hydrocarbons in the cold.

Towards reducing agents such as sodium amalgam and water, tin and hydrochloric acid, sodium and boiling alcohol, which yield nascent hydrogen, as well as towards ordinary hydrogen either alone or in presence of a catalyser, these hydrocarbons are also absolutely inert. In these respects they differ from the members of certain classes of hydrocarbons with which we shall meet later.

Since the members of the series $\text{C}_n\text{H}_{2n+2}$ are incapable of taking up more hydrogen and of giving rise to such compounds as CH_5 or C_2H_7 they are known as Saturated Hydrocarbons.

This inability to combine directly with more hydrogen goes hand in hand with the fact that although halogens can give rise to substitution products of the paraffin hydrocarbons (see page 4) in which the total number of univalent atoms or radicals attached to carbon remains four, substances such as CH_4Br , $\text{C}_2\text{H}_6\text{Br}$ are never obtained by the action of halogens on members of the series $\text{C}_n\text{H}_{2n+2}$.

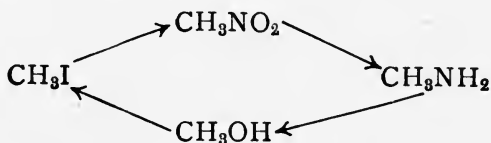
A more complete list of the most important members of the paraffin or $\text{C}_n\text{H}_{2n+2}$ series may now be appended, and it will be instructive for the student to note the gradation in physical properties which is observed as the series is ascended. The table refers only to those hydrocarbons possessing a normal structure.

C_nH_{2n+2} HYDROCARBONS.

Formula.	Name.	Melting-point.	Boiling-point.	Specific gravity.
CH_4	Methane	-186°	-160°	0.415 (at -160°)
C_2H_6	Ethane	-172.1°	-93°	0.446 (at 0°)
C_3H_8	Propane	—	-45°	0.536 (at 0°)
C_4H_{10}	Butane	-135°	-0.1°	0.600 (at 0°)
C_5H_{12}	Pentane	-130.8°	36.3°	0.627 (at 14°)
C_6H_{14}	Hexane	-94.03°	68.9°	0.658 (at 20°)
C_7H_{16}	Heptane	-97.1°	98.4°	0.683 „
C_8H_{18}	Octane	-56.5°	125.6°	0.702 „
C_9H_{20}	Nonane	-51°	149.5°	0.718 „
$C_{10}H_{22}$	Decane	-31°	173°	0.730 „
$C_{11}H_{24}$	Undecane	-26°	194°	0.774 (at melting-point)
$C_{12}H_{26}$	Dodecane	-12°	214.5°	0.773 „ „
$C_{14}H_{30}$	Tetradecane	4°	252.5°	0.775 „ „
$C_{16}H_{34}$	Hexadecane	18°	287.5°	0.775 „ „
$C_{20}H_{42}$	Eicosane	36.5°	205^*	0.7775 „ „
$C_{21}H_{44}$	Heneicosane	40.1°	215°	0.7778 „ „
$C_{23}H_{48}$	Tricosane	47.4°	234°	0.7799 „ „
$C_{31}H_{64}$	Hentriacontane	68.4°	302°	0.7799 „ „
$C_{35}H_{72}$	Pentatriacontane	74°	331°	0.7813 „ „
$C_{60}H_{122}$	Hexacontane	101°	—	—

* At 15 mm. pressure, and the same for those following.

Now, it will have been noted that the chlorination product of methane, the constitution of which is represented by the formula CH_3Cl and of which the rational name would obviously be monochloromethane, is also known as methyl chloride, similarly moniodomethane as methyl iodide. As we shall see later, the group or radical— CH_3 is capable of passing unchanged through many reactions in which it functions as if it were a univalent atom, thus—



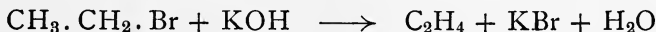
By analogy the group C_2H_5 —in bromoethane (ethyl bromide) is known as ethyl, and in general the group C_nH_{2n+1} derived from a hydrocarbon C_nH_{2n+2} is known as an Alkyl radical. Each radical has a special name derived by substituting -yl for -ane in the name of the corresponding hydrocarbon.

It must be clearly understood, however, that the alkyl

radicals are not capable of independent existence. In any reaction which might at first sight be expected to yield them, hydrocarbons C_nH_{2n+2} are always obtained, with twice as many carbon atoms in the molecule as would be present in the radical under consideration, *e.g.* the action of sodium on ethyl iodide C_2H_5I does not yield "ethyl," but normal butane C_4H_{10} .

UNSATURATED HYDROCARBONS.

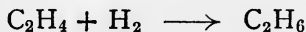
Olefine Hydrocarbons.—If ethyl bromide $CH_3 \cdot CH_2 \cdot Br$ be treated with an alcoholic solution of potassium hydroxide, commonly known as alcoholic potash, a gas is evolved which on analysis is proved to have a constitution represented by the formula C_2H_4



This gas is known as ethylene, or olefiant gas, it is readily inflammable and possesses certain properties which sharply distinguish it from methane.

Thus, when brought into contact with bromine the red colour is immediately discharged, oily drops of ethylene dibromide separate out on the sides of the vessel,* and most important of all, no hydrogen bromide is produced. When bromine and methane interact, the reaction proceeds slowly, except in the presence of direct sunlight, and as we know, hydrogen bromide is produced.

Similarly, if ethylene be mixed with hydrogen and passed through a hot tube containing finely divided metallic nickel, hydrogen enters into combination with the hydrocarbon, and the issuing gas contains ethane



No such behaviour is exhibited by methane. The action of the nickel will be discussed in Chapter XVII.

Finally, ethylene reduces potassium permanganate and combines with sulphuric acid. The nature of the products formed will be discussed after the formula of ethylene has been derived.

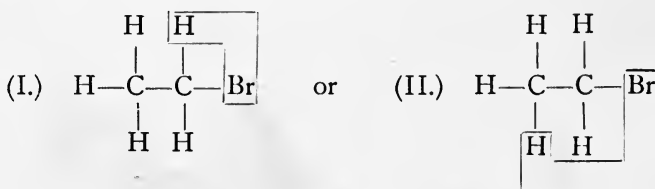
* Hence the name olefiant gas.

UNSATURATED HYDROCARBONS OF THE ETHYLENE SERIES (OLEFINES).

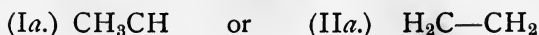
Name.	Formula.	Boiling-point.
Ethylene	C_2H_4	- 103°
Propylene	C_3H_6	- 48°
n-Butylene	C_4H_8	- 5°
n-Amylene	C_5H_{10}	39°
Hexylene	C_6H_{12}	68°
Heptylene	C_7H_{14}	98°
Octylene	C_8H_{16}	124°
Nonylene	C_9H_{18}	153°
Decylene	$C_{10}H_{20}$	172°
Undecylene	$C_{11}H_{22}$	195°

Constitution of Ethylene.—Any formula which may be proposed to express the constitution of ethylene must be capable of clearly indicating the fundamental difference in properties which distinguishes this gas from the corresponding saturated compound containing two atoms of carbon, ethane.

It is obvious that the formation of ethylene from ethyl bromide is accompanied by the elimination of hydrogen bromide. This may be represented in two ways—



Ethylene might therefore be represented by two possible formulæ—

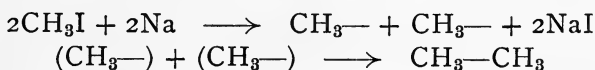


According to formula (Ia.) carbon can be divalent, and according to (IIa.) can be tervalent. In either case the readiness with which hydrogen, chlorine or bromine are added could be ascribed to the tendency for di- or tervalent carbon to assume the quadrivalent condition.

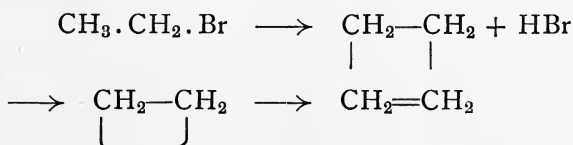
If (Ia.) represent the constitution of ethylene the product obtained by the addition of chlorine would have the constitution $\text{CH}_3 \cdot \text{CHCl}_2$. Now, a compound which undoubtedly possesses this constitution has been prepared by another method, and is found not to be identical with ethylene

dichloride. The formula $\text{CH}_3 \cdot \text{CH}$ does not therefore represent the constitution of ethylene.

If the production of ethylene from ethyl bromide be represented by scheme (II.) it will be seen that after the elimination of HBr each carbon atom is left with one unsatisfied bond. Now, we have seen before that when reactions take place which might conceivably give rise to the formation of compounds containing carbon atoms with free bonds (*e.g.* action of sodium on methyl iodide) the free bond on one carbon atom unites with that on another, thus—



Now, if we suppose that in the preparation of ethylene from ethyl bromide the free affinities of each of the two carbon atoms mutually satisfy each other, we arrive at a formula for ethylene which assumes that the two carbon atoms are doubly linked—



It is not to be inferred from this that in ethylene (or in the many other compounds in which similar "double bonds" are to be assumed) the two carbon atoms are more firmly united with each other than are ordinary singly bound carbon atoms. The reverse is rather the case—the double bond represents a weak point in the molecule.

From what has been said it should be obvious that when ethylene and similar compounds take up two atoms of hydrogen or bromine to form ethane or ethylene dibromide respectively, only the doubly linked carbon atoms participate in the reaction.

In the compounds thus produced the free affinities of the carbon atoms which previously mutually satisfied each other thus forming the double bond, are now satisfied with hydrogen or bromine, with the result that the ordinary single $\text{C}-\text{C}-$ linkage is re-established.

The phenomenon can also be regarded as a rupture of the double bond under the influence of the reagent, with the consequent production of free affinities which are then immediately satisfied with bromine or other halogen or hydrogen.

Since ethylene and its homologues combine so readily with hydrogen and the halogens (their behaviour being thereby strikingly differentiated from that of the hydrocarbons C_nH_{2n+2}) they are known as "unsaturated" compounds.

The process of combination of such compounds with hydrogen, the halogens, etc., is known as "addition," and the substances which result are designated addition products.

The difference between "addition" and "substitution" is of fundamental importance, and must be thoroughly grasped.

It is a perfectly general rule that all unsaturated compounds are oxidized by potassium permanganate, which is itself decolorized. This reaction therefore is largely used as a test for the presence of double linkings. As would naturally be expected the oxidation begins at the weakest point of the molecule, namely, at the unsaturated linkage, and frequently the compound splits at the double bond, forming two new substances.

The products of oxidation vary, however, with the conditions of the experiment, *e.g.* duration of interaction, temperature, concentration of the permanganate, etc. When ethylene and numerous similarly constituted compounds are treated with cold, one per cent. potassium permanganate solution glycol or substituted glycols are obtained (see page 86).

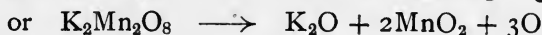


A substituted glycol.

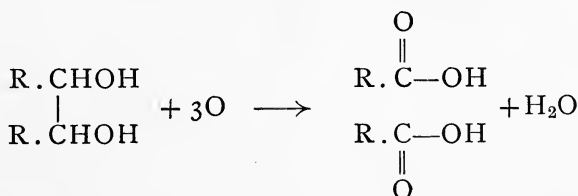
Glycols are also obtained by the action of hydrogen peroxide on certain unsaturated compounds. It may at first sight appear strange that the action of potassium permanganate should result in the addition of the elements of hydrogen peroxide to the double bond.

In neutral solution two gram molecules of potassium permanganate are capable of giving up three atoms of oxygen, while potassium hydroxide and manganese dioxide are simultaneously produced.

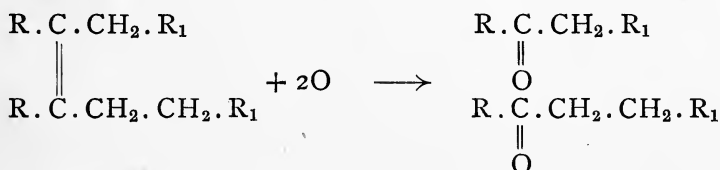
The formation of glycols can then readily be understood if we consider that one gram molecule of water, and one gram atom of nascent oxygen enter into reaction with each gram molecule of a singly unsaturated hydrocarbon, *i.e.* one which contains only one double bond, thus—



The glycols which are thus obtained are often unstable and undergo further oxidation, acids being formed.



On the other hand, the permanganate may oxidize some of the unsaturated hydrocarbon to ketones (see page 33).



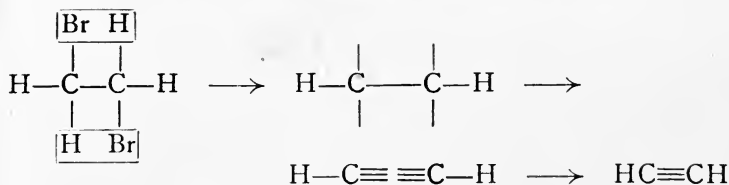
If R and R₁ are different, each of these ketones may give rise in contact with the permanganate to four distinct acids, so it is easily seen that the reaction between potassium permanganate and an unsaturated hydrocarbon may be extremely complicated.

Acetylene Hydrocarbons.—We can now pass to the consideration of another homologous series of unsaturated hydrocarbons, namely, that of which the well-known gas acetylene forms the first member, and in the molecules of which the relations of the constituent atoms may best be expressed by the hypothesis that some of them are united by triple bonds.

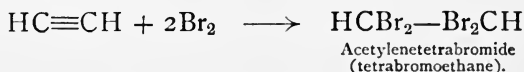
When ethylene dibromide is treated with alcoholic potash two molecules of hydrogen bromide are eliminated, thus—



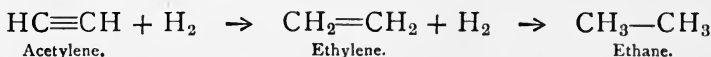
As in the formation of ethylene, we may assume that free bonds are left on each carbon atom after the removal of the hydrogen bromide. In this case there will be two free bonds on each carbon atom, which will then unite and mutually satisfy each other, the two carbon atoms being henceforth united by a triple bond, thus—



Triple bonds between carbon atoms would, on the analogy of ethylenic compounds, probably form a weak spot in the molecule of the compound. We need not therefore be surprised to find that acetylene and its homologues are characterized by considerable additive powers towards, *e.g.* hydrogen, the halogens, the halogen hydrides, and even water. Acetylene combines directly with bromine—



In presence of reduced nickel, the reaction with hydrogen takes place in two stages—

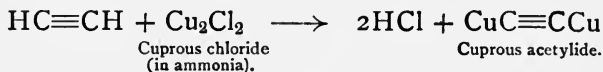


In presence of certain mercury salts water is added on—

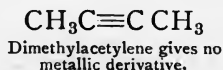
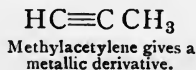


Other compounds, not necessarily hydrocarbons, which contain a triple bond, are able to take up the elements of water under the influence of concentrated sulphuric acid.

Another property which is very characteristic of some acetylene hydrocarbons is their power of forming metallic derivatives (see page 87). Thus—



It may be mentioned that although practically all hydrocarbons containing triply bound carbon atoms add on bromine and hydrogen under suitable conditions, yet it is only those which contain hydrogen atoms directly linked to such carbon atoms that are capable of yielding metallic derivatives; *e.g.*—

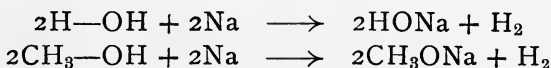


ALCOHOLS.

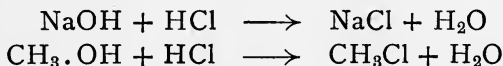
When methyl iodide is treated with moist silver oxide (in which we must assume the presence of silver hydroxide AgOH), a reaction takes place in which silver iodide and a substance known as methyl alcohol are produced.

Methyl alcohol is found to have a composition represented by the formula CH_4O . Since moist silver oxide contains an $-\text{OH}$ group, just as do sodium and potassium hydroxides, and as the reaction seems to be a double decomposition, it would appear probable that the new compound CH_4O might have the constitution CH_3OH , and possess some of the properties usually associated with metallic hydroxides or even with water.

This is found to be the case ; with sodium, hydrogen is evolved and the reaction would appear to be analogous with that of water on sodium, thus—



Again, methyl alcohol reacts with hydrogen chloride in a manner analogous with the behaviour of sodium hydroxide, and gives rise to monochloromethane



The halogen derivatives (the iodides are most convenient for the purpose) of all aliphatic hydrocarbons react in a similar way with AgOH , in each case giving rise to a compound containing an $-\text{OH}$ group in place of the halogen atom and having some of the properties of a hydroxide.

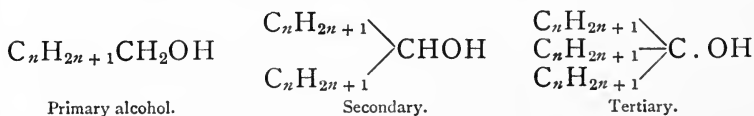


All these alcohols, as they are called, contain only one atom of hydrogen replaceable by metals, namely, that in the $-\text{OH}$ group. This atom, therefore, has properties entirely different from the hydrogen atoms of the alkyl radical.

The term "alcohol" is used in organic chemistry to denote a compound containing the group $\text{C}-\text{OH}$, except when the

carbon atom forms part of a benzene ring, when the substance in question is known as a phenol or when the $-\text{OH}$ is present in $-\text{CO}.\text{OH}$ the carboxyl group (see p. 31).*

It will be seen that three types of alcohols exist, accord-



ing as to whether the hydroxyl group is attached to a primary, secondary, or tertiary carbon atom.

On treatment with phosphorus pentachloride PCl_5 the $-\text{OH}$ group of practically all alcohols is replaced by a chlorine atom.

Homologous series of primary, secondary and tertiary alcohols are, of course, known. The lower members of the first series are mobile, inflammable liquids with a burning taste, the middle ones thicker liquids immiscible with water, while the higher members, such as cetyl alcohol $\text{C}_{16}\text{H}_{33}\text{OH}$ obtained from spermaceti, are solids with low melting-points.

THE NORMAL ALCOHOLS OF THE SERIES $\text{C}_n\text{H}_{2n+1}\text{OH}$.

Name.	Formula.	Melting-point.	Boiling-point.	Specific gravity. at 0° .
Methyl alcohol . .	CH_3OH	-97.1°	67.4°	0.812
Ethyl alcohol . .	$\text{C}_2\text{H}_5\text{OH}$	-114.15°	78°	0.806
Propyl alcohol . .	$\text{C}_3\text{H}_7\text{OH}$	—	96.5°	0.817
Butyl alcohol . .	$\text{C}_4\text{H}_9\text{OH}$	-79.6°	116.7°	0.823
Amyl alcohol . .	$\text{C}_5\text{H}_{11}\text{OH}$	—	137°	0.829
Hexyl alcohol . .	$\text{C}_6\text{H}_{13}\text{OH}$	—	157°	0.833
Heptyl alcohol . .	$\text{C}_7\text{H}_{15}\text{OH}$	-36.5°	175°	0.836
Octyl alcohol . .	$\text{C}_8\text{H}_{17}\text{OH}$	-17.9°	194.5°	0.839
Nonyl alcohol . .	$\text{C}_9\text{H}_{19}\text{OH}$	—	213°	0.842

* A substance such as tartaric acid, $\text{HO}.\overset{\text{O}}{\underset{\text{O}}{\text{C}}}.\text{CHOH}.\text{CHOH}.\overset{\text{O}}{\underset{\text{O}}{\text{C}}}.\text{OH}$, is both an acid and an alcohol.

THE ISOMERIC PROPYL, BUTYL, AND AMYL ALCOHOLS.

Name.	Formula.	Melting-point.	Boiling-point.	Specific gravity at 20°.
Propyl alcohols C_3H_8O —				
1. Normal	$CH_3 \cdot CH_2 \cdot CH_2OH$	glass-like	97°	0·804
2. iso	$CH_3 \cdot CHOH \cdot CH_3$	— 85·8°	81°	0·789
Butyl alcohols $C_4H_{10}O$ —				
1. Normal primary . . .	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	— 79·6°	117°	0·810
2. Normal secondary . .	$CH_3 \cdot CH_2 \cdot CHOH \cdot CH_3$	glass-like	100°	—
3. iso	$(CH_3)_2CH \cdot CH_2OH$	glass-like	107°	0·806
4. Trimethylcarbinol . .	$(CH_3)_3C \cdot OH$	25·5°	83°	0·786
Amyl alcohols $C_5H_{12}O$ —				
1. Normal primary . . .	$CH_3 \cdot (CH_2)_3 \cdot CH_2OH$	—	138°	0·815
2. iso Butylcarbinol . .	$(CH_3)_2CH \cdot CH_2 \cdot CH_2OH$	— 134°	131°	0·810
3. Secondary butylcarbinol	$CH_3 \cdot CH(C_2H_5) \cdot CH_2OH$	—	128°	—
4. Methylpropylcarbinol .	$CH_3 \cdot (CH_2)_2 \cdot CHOH \cdot CH_3$	—	119°	—
5. Methylisopropylcarbinol	$(CH_3)_2CH \cdot CHOH \cdot CH_3$	—	112·5°	—
6. Diethylcarbinol . . .	$C_2H_5 \cdot CHOH \cdot C_2H_5$	—	117°	—
7. Dimethylethylcarbinol .	$(CH_3)_2C(OH) \cdot C_2H_5$	—	102°	—
8. Tertiary butylcarbinol .	$(CH_3)_3C \cdot CH_2OH$	—	112°	—

Optical Activity.—From a consideration of the constitutional formulæ it will be seen that there are four structurally possible butyl alcohols. All of these have been prepared and fairly thoroughly investigated. Their structural formulæ are indicated on page 20.

It was found, however, that one of these alcohols, namely, normal secondary butyl alcohol, could, by suitable means, be separated into two other distinct forms, so that the number of isomers of this butyl alcohol is three, making a total of six butyl alcohols in all.

This isomerism is, however, totally different from that which we have considered up to the present.

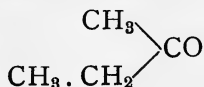
So far we have been accustomed to consider isomerism as always being accompanied by differences in chemical constitution, and frequently in melting-point, boiling-point and other physical properties.

If, however, we study the properties of the two new alcohols into which normal secondary butyl alcohol can be separated, we shall find—

(i) Their boiling-points, melting-points and solubilities are identical.

(ii) Their specific gravities are the same.

Moreover on oxidation each of the *three* alcohols gives rise to the same substance—methyl ethyl ketone.



When reduced with hydriodic acid they are all three converted into the same hydrocarbon, namely normal butane.

In one particular, however, the three alcohols differ. The first, from which by suitable methods the other two can be obtained, is found to be without action on polarized light.

When a beam of plane polarized light is passed through layers of these alcohols,* the plane of polarization is rotated by one isomer to the left (*lævo*-rotation) by another to the right (*dextro*-rotation), while the other exercises absolutely no effect.†

The first two alcohols are therefore said to be optically active, the other optically inactive, and the three are spoken of as optical isomers.

It is found that a very large number of organic compounds are optically active, so that the phenomenon is a very general one.

When the three alcohols are esterified (see page 37) with acetic acid three secondary butyl acetates are produced which differ from each other in the same way that the original alcohols do, namely, in their action on polarized light.

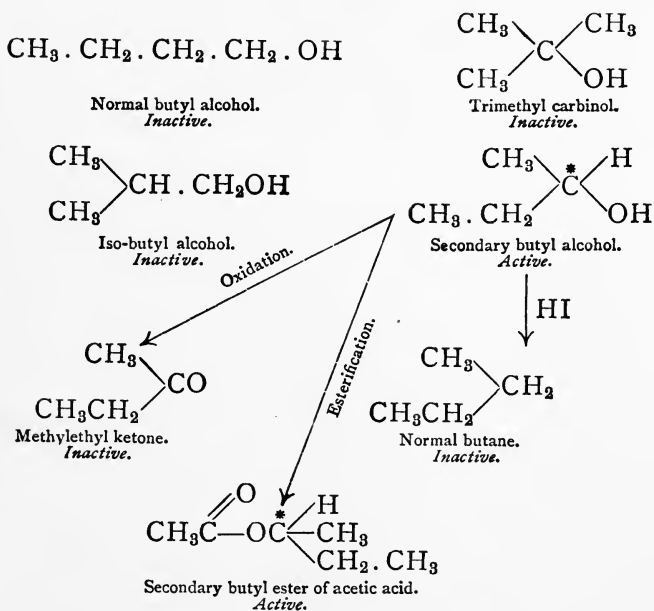
The different effect produced on a beam of plane polarized light by optical isomers is not due to differences in the arrangement of the *molecules* of the substances about one another, as in quartz, which is optically active, since the optical activity of liquids is found to persist even in the vaporous condition, in which state, according to the kinetic theory of gases, any stable arrangement of the molecules is quite impossible.

We must, therefore, carefully examine the structural formula of the butyl alcohol mentioned above, which is capable, to employ the customary expression, of being resolved into its optically active components. It is possible that such an examination will bring to light some point in which the alcohol in question is unique.

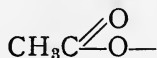
If such should be the case it will be necessary for us to determine whether the point of difference we have discovered is sufficient to account for the phenomenon of optical activity. Above all, we must carefully study the behaviour towards polarized light of the various products into which our active butyl alcohol may be converted—

* For this purpose an apparatus known as a polarimeter is employed, for a description of which the reader is referred to text-books of physical chemistry, where he may also find an account of the theoretical considerations underlying the phenomenon of polarization.

† As a rule, although the specific gravities, solubilities, melting-points and boiling-points of optical isomers, *i.e.* the *dextro*-rotatory and *lævo*-rotatory modifications, are similar, these constants differ from those of the inactive form.



If we now inspect the various formulæ given above, we shall find that both the optically active compounds, namely, secondary butyl alcohol and the ester which this alcohol forms with acetic acid are unique in one particular. They each contain a carbon atom (indicated by an asterisk) which is linked to *four different atoms or groups of atoms*. In the alcohol these are CH_3 —, CH_3CH_2 —, H —, and HO —. In the ester instead of HO — we have—



The molecules of the other substances of which the formulæ are given do not contain such carbon atoms. If we afterwards examine the formulæ of most other optically active compounds we shall find that the molecules of these substances contain at least one carbon atom linked to four different groups. Such an atom is known as an *asymmetric carbon atom*.†

Before turning to consider how this conception of the

† Optically active compounds containing asymmetric atoms of silicon, nitrogen, phosphorus, sulphur, selenium and tin, instead of asymmetric carbon are also known.

asymmetric carbon atom helps us to understand the occurrence of optical activity in compounds containing it, it should be mentioned that the pure lævo-rotatory form of an optically active substance rotates the plane of polarization to an extent exactly equal to, but different in *sign* from, that to which the plane of polarization is rotated by the pure dextro-rotatory form. We now see why a mixture of the dextro (*d*-) and lævo (*l*-) forms in equal amounts is completely inactive.

It was stated on page 2 that the doctrine of the quadrivalence of the carbon atom forms the basis of theoretical organic chemistry. A large amount of discussion has taken place as to the manner in which the four affinities of carbon (and in general the affinities of all atoms) are distributed on the surface of the atom. The distribution of the affinity probably differs for atoms of differing valency.

In the case of carbon the only assumption which can be shown to be in agreement with observed facts is that the affinities or valencies of the atom are directed towards the angles of a regular tetrahedron of which the carbon atom forms the centre. In order thoroughly to understand the reasoning into which we must now enter, it is desirable that models of carbon atoms be constructed. A sphere may be cut out of a cork to represent the carbon atom. The bonds or affinities may be represented by needles or wires stuck into the cork and directed towards the angles of an imaginary regular tetrahedron. Other cork spheres of different colours may now be attached to these wires to represent various atoms which have entered into combination with the carbon atom.

Let us consider the compounds CA_2B_2 , CA_2BE , and CA_3E . If element A be represented by red corks, B by blue, and E by yellow, for the compound CA_2B_2 we shall have two red corks and two blue ones attached to the four needles of the carbon atom C, and so on. Let us make two models of CA_2B_2 with the groups A and B in different positions. We shall find that by rotating the models we can get the similar groups to coincide, in other words, we cannot construct two models of the compound CA_2B_2 which shall possess different configurations. That is to say, we should not expect to find that a compound of this type could exist in isomeric forms, and experience confirms this expectation.

Similarly, if we make two models of the compound CA_2BE and two of CA_3E , we shall be able by rotating them to get the like groups into similar positions, and as might be expected, we do not meet with isomerism in compounds of these types.

If, however, we make two models of a compound of the type CABDE in which the relative positions of A, B, D and E are different, we shall find that two configurations are possible, the like groups of which cannot be made to coincide. The two configurations resemble one another as an object and its mirror image, or as a right-hand and left-hand glove. We might, therefore, expect compounds of this type to exist in two modifications, which would exhibit certain differences in properties. This, as we have seen, is borne out by experiment, and the only difference between them consists in their effect on polarized light.

The arrangement of the groups round the asymmetric carbon atom gives rise in some way to the action on polarized light, and from the relation which we have found to exist between the two possible configurations, we can see in a general way how it is that the two optically active isomers produce rotations arithmetically equal but opposite in algebraical sign.

Another very important consideration dealing with the question of optically active compounds must now be mentioned.

Large numbers of these substances occur in nature, in plant tissues, juices, seeds, etc., and in the tissues of men and animals.

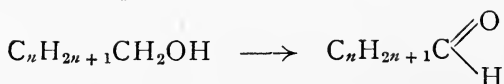
On the other hand, if we attempt to synthesize an optically active substance in the laboratory we always obtain as a result the inactive substance, *i.e.* a mixture of equal amounts of the dextro- and the lævo-rotatory forms. Special methods for the separation of these must be employed if the optically active substances are to be obtained.

This is probably due to the fact that in any chemical reaction carried out in the laboratory there is just as much probability of the formation of the *d*- as of the *l*- modification. Consequently, both are formed in equal quantities.

In nature some particular agency must be present which is lacking under laboratory conditions. As to the nature of this agency we know practically nothing.

The extraction of an optically active substance from a naturally occurring product indicates that that substance has its origin in animal or vegetable tissue (see page 74).

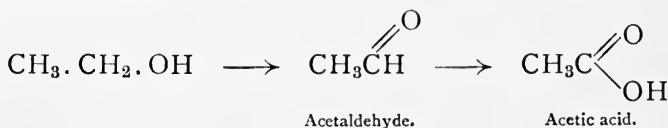
Properties of the Aliphatic Alcohols.—On oxidation with chromic acid solution or by incomplete combustion, two hydrogen atoms are removed and volatile compounds known as aldehydes are formed—



The aldehydes, on further oxidation, are converted into acids.



It will be seen that the aldehyde and the acid both contain the same number of carbon atoms as the alcohol, *e.g.* ethyl alcohol when treated with chromic acid yields acetaldehyde which on standing in air or by oxidation with potassium permanganate or more chromic acid is converted into acetic acid—

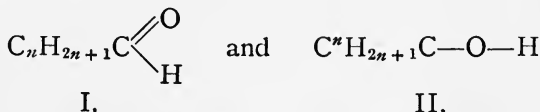


ALDEHYDES.

We may now deal with the oxidation of the primary alcohols. The first products obtained are aldehydes, most of which are colourless liquids (formaldehyde is a gas) with a peculiar pungent odour which is in some cases reminiscent of fruit extracts.

The aliphatic aldehydes have the general formula $\text{C}_n\text{H}_{2n}\text{O}$. They contain no hydrogen replaceable by sodium, so the hydroxyl group is absent; a further proof of this is furnished by the action of phosphorus pentachloride, which instead of introducing one chlorine atom into the molecule in place of hydroxyl replaces the oxygen atom by two atoms of chlorine.

The oxygen in aldehydes is therefore differently linked from that in alcohols. It can be shown that the alkyl group of a primary alcohol $\text{C}_n\text{H}_{2n+1}\text{CH}_2\text{OH}$ is present unchanged, in the aldehyde derived therefrom,* which must therefore possess one of the two formulæ—



* This, of course, is only true if the formula be written as above, since the terminal $-\text{CH}_2$ group linked to hydroxyl is oxidized to CHO . Thus the methyl group of ethyl alcohol appears in acetaldehyde, but not the ethyl radical.

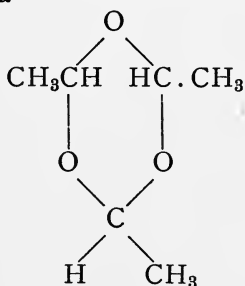
The absence of an —OH group has, however, been proved, so that the general formulæ for aldehydes must be written as I. The adoption of the second would obviously, moreover, lead to difficulties as to the valency of carbon.

Properties of the Aldehydes.—As has already been mentioned, they are very readily oxidized and so are capable of reducing silver salts to metallic silver, alkaline copper solutions to cuprous oxide and potassium permanganate to hydrated manganese dioxide.

Towards both acids and alkalis they are very sensitive.

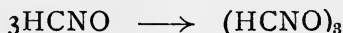
Acetaldehyde (so called because on oxidation it yields acetic acid, compare propionaldehyde and propionic acid, etc.), is a liquid boiling at 24°C . On addition of a few drops of sulphuric acid it is converted into a colourless liquid boiling at 124°C . having the same percentage composition and empirical formula, but of which the vapour density indicates that the formula $(\text{C}_2\text{H}_4\text{O})_3$ must be ascribed to it. This compound is known as paracetaldehyde, or more shortly, paraldehyde.

The cyclic formula—



is believed to represent its constitution since on distillation with dilute acid, it breaks up again into acetaldehyde. Now, experience has shown that the linkage $\text{C}—\text{C}$ is much more difficult to break than the linkage $\text{C}—\text{O}—\text{C}$, so in view of the instability of paraldehyde the carbon atoms are supposed to be linked through oxygen.

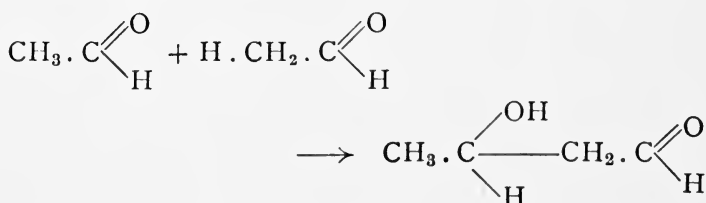
When the molecules of a substance combine to form a body having the same percentage composition and from which the original compound can readily be regenerated, the change is known as Polymerization and the compound which results is called a polymer of the original one. Paraldehyde is a polymer of acetaldehyde. Other examples of polymerization are the production of (I) cyanuric acid from cyanic acid



(II) Paraformaldehyde from formaldehyde—



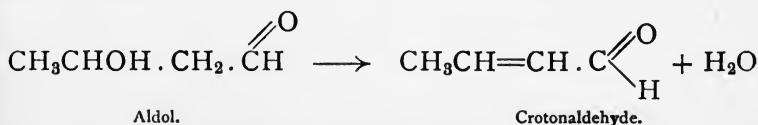
Under the influence of dilute alkalis most aldehydes (except formaldehyde) are converted into substances known as aldols, one molecule of water being eliminated from two molecules of the aldehyde. From these aldols the original aldehyde cannot be regenerated. This renders it highly probable that the union of the aldehyde molecules takes place through C—C linkings. The conversion under suitable conditions of aldols into straight chain saturated acids of the series $\text{C}_n\text{H}_{2n+1}\text{COOH}$ proves this to be the case. The formation of ordinary aldol from acetaldehyde is to be represented thus—



When two or more molecules of a substance unite *through carbon bonds* to produce a compound from which the original compound cannot readily be regenerated, the process is known as Condensation.

Examples of this phenomenon are the condensation of acetone to mesitylene (page 231) and of acetylene to benzene (page 229).

Since aldol contains an aldehyde grouping— $\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$ it can itself undergo another aldol condensation, thus yielding a compound containing a chain of eight carbon atoms which can then condense to a chain of sixteen atoms, and so on. Moreover, aldol can lose water, forming unsaturated compounds thus—



These two reactions are probably responsible for the

formation of a yellow resin when aldehyde solutions are boiled with caustic soda solution. See also section on sugars.

CARBOHYDRATES.

The compounds known as carbohydrates all possess the general formula $C_n(H_2O)_x$. The name arises from the fact that in all these compounds hydrogen and oxygen were found to be present in the ratio in which they combine to form water. It should be unnecessary to state that they cannot be formed by the action of carbon on water.

Carbohydrates may be divided into three classes: the complex carbohydrates such as cellulose,* starch, glycogen, inulin, and dextrin; the relatively simpler ones, such as cane sugar and milk sugar, and the simplest such as fructose, glucose, and xylose. The first two classes are known as polysaccharides, the last class as monosaccharides. The polysaccharides, as we shall see later, yield simpler sugars on boiling with acids, the monosaccharides are unchanged.

Those polysaccharides which under these conditions yield two molecules of a monosaccharide are known as disaccharides. The monosaccharides may be tetroses, pentoses, or hexoses according as there are four, five, or six carbon atoms in the molecule. Some of the monosaccharides are ketones such as fructose, others are aldehydes, *e.g.* glucose.

Starch.—The presence of this substance in potatoes, rice, and various cereals is well known. The starch granules from different plants, although possessing the same chemical composition, appear sharply differentiated when viewed under the microscope. These differences, however, are purely physical in their nature, and are due to the varying manner in which the starch has been deposited and stored up by the various plants. The empirical formula of starch is $C_6H_{10}O_5$. Its molecular weight, however, is unknown, but is undoubtedly very great, so that the molecule of starch is usually represented as $(C_6H_{10}O_5)_n$. It is interesting to note that while starch is stored up to a large extent in the tissues of many plants, and inulin occurs in others, for example, in the tubers of the dahlia, glycogen occurs in large quantities in the livers of men and animals, and forms a valuable reserve store of energy.

Starch does not dissolve in cold water, but on boiling forms a turbid colloidal solution. The characteristic dark-

* For information regarding cellulose, see page 260.

blue colour which is produced when this "starch paste" is treated with a solution of iodine in potassium iodide is well known. On boiling the solution the colour is discharged, but returns on cooling. Inulin does not give this reaction, and glycogen produces under similar conditions a brown coloration.

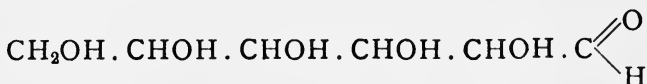
If starch be heated to about 200°C ., or boiled for a short time with dilute acids, it is converted into a substance known as dextrin. This substance, which is largely used as an adhesive under the name British gum, is of relatively small importance chemically. Its properties are intermediate between those of starch and the important class of compounds which must next be considered, namely the sugars.

Sugars.—If the boiling with dilute acids be continued for long it is found that the starch is completely converted into a substance known as glucose or grape sugar, which is incapable of giving rise to a blue coloration with a solution of iodine in potassium iodide. After removal of the acid the glucose can be obtained in the solid form. It is also produced by the action of certain enzymes on starch. Both these methods of preparation are more fully discussed in Chapter XVIII.

Glucose, dextrose, or grape sugar has the molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$, as is indicated by analysis, and the depression of the freezing-point of its aqueous solutions. It is therefore a hexose. Its formation from starch may be expressed thus—



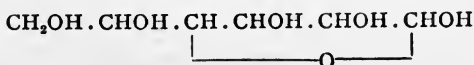
When quite pure, glucose is a white crystalline solid, very soluble in water, and possessing a slightly sweet taste. The structural formula—



has been assigned to it on the following grounds.*

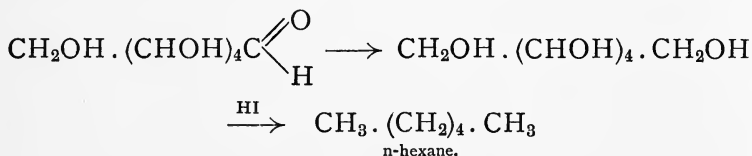
(i) It shows the reactions of aldehydes, *e.g.* the reduction of Fehling's solution, resinification with alkalis, formation of an addition compound with hydrocyanic acid, and is therefore an aldo-hexose.

* Certain observations, into the details of which we cannot enter here, have led to the proposal of another formula for glucose—

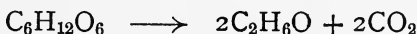


(ii) Glucose forms a penta-acetate and must therefore contain five hydroxyl groups.

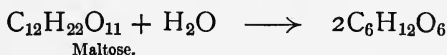
(iii) On reduction it takes up two atoms of hydrogen, as do most aldehydes, and is converted into an alcohol which can be made to yield a hexa-acetate; with hydriodic acid this hexahydric alcohol finally yields normal hexane. Glucose therefore contains a straight chain of six carbon atoms—



In presence of living yeast-cells, or of the enzyme which they secrete, glucose is converted into alcohol and carbon-dioxide, traces of succinic acid, glycerol, and amyl alcohol being produced at the same time.



Glucose is also obtained by the action of dilute acids on such substances as cane sugar, milk sugar, and malt sugar, whose names sufficiently indicate their modes of occurrence. These three substances are isomeric since they all possess the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Their conversion into glucose through interaction with water in presence of dilute acids is expressed thus—



This reaction resembles the conversion into glucose of the more complex substance starch, and both furnish examples of a phenomenon known as *hydrolysis*, which may be defined as “decomposition brought about by reaction with one or more molecules of water.”

It is important to note, however, that glucose is not the only product obtained when dilute acids act on cane sugar. Another sugar known as fructose, fruit sugar, or lævulose is produced which also has the formula $\text{C}_6\text{H}_{12}\text{O}_6$. As a result of researches, which cannot be fully described here, the constitutional formula—



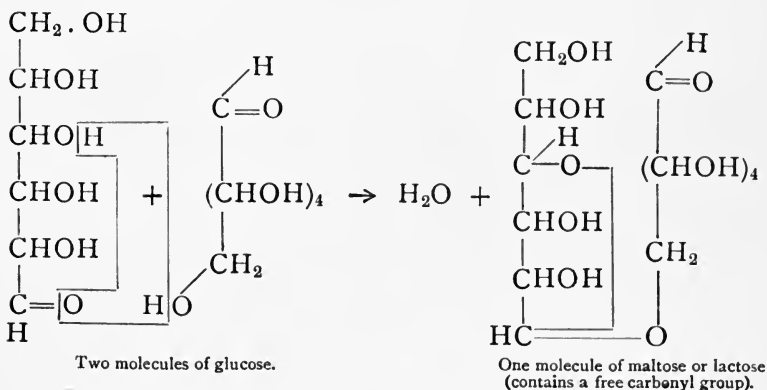
has been assigned to it. It is clearly a keto-hexose, since it contains the group CO, characteristic of ketones (see page 33).

Cane sugar would therefore appear to be formed by the union of a glucose with a fructose molecule, with the simultaneous elimination of one molecule of water. It is therefore a disaccharide. Similarly, it can be shown that malt sugar consists of two glucose molecules minus one molecule of water, and that milk sugar is similarly produced from glucose and another hexose known as galactose.

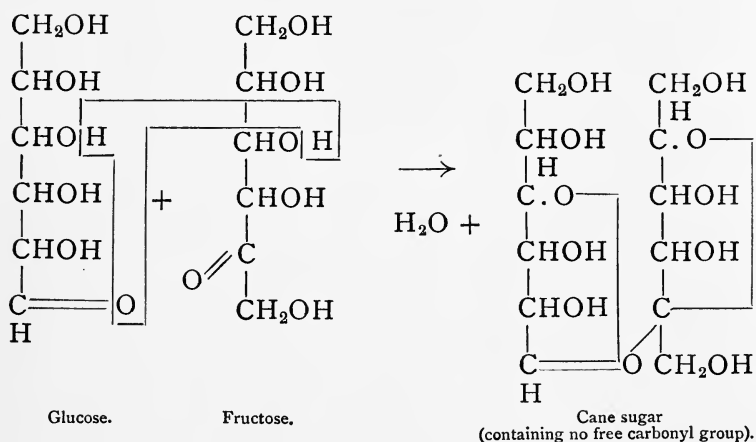
Now although both glucose and fructose reduce Fehling's solution, giving rise to a red precipitate of cuprous oxide, cane sugar does not do so.

It would therefore appear that cane sugar contains no free carbonyl group.

On the other hand, lactose or milk sugar and maltose or malt sugar readily reduce Fehling's solution. The formulæ for maltose and cane sugar indicated below have been put forward to explain the observed reactions of these substances. As regards the constitution of the molecules of the more complex carbohydrates such as starch, glycogen, and cellulose very little is known.



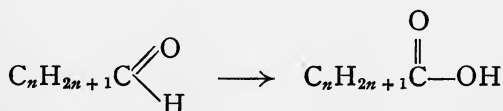
Similarly, the constitution of cane sugar, which is formed from a molecule of glucose and a molecule of fructose, is represented thus—



It may be mentioned that starch and cellulose do not exhibit the reactions of ketones or aldehydes. Free carbonyl groups are therefore absent from their molecules. The chemical composition of starch and cellulose therefore is probably somewhat similar to, but much more complex than, that of cane sugar.

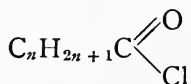
ACIDS.

The acid obtained by the oxidation of a primary saturated alcohol $\text{C}_n\text{H}_{2n+1}\text{OH}$ contains the same number of carbon and hydrogen atoms, but one extra atom of oxygen. The alkyl group of the primary alcohol $\text{C}_n\text{H}_{2n+1}\text{CH}_2\text{OH}$ can be proved to be present unchanged in the acid $\text{C}_n\text{H}_{2n+1}\text{COOH}$ and as it is also present in the aldehyde $\text{C}_n\text{H}_{2n+1}\text{C}\begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix}$ (see footnote, page 23), it follows that the change from an aldehyde to the corresponding acid should be represented thus—



This formulation is confirmed by the fact that all the acids react with sodium evolving hydrogen and giving rise to monosodio-derivatives, while with phosphorus pentachloride

one atom of oxygen and one of hydrogen are replaced by one chlorine atom giving rise to a compound of the formula—

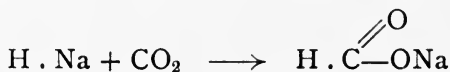
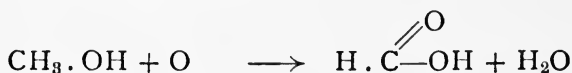


These reactions we have learnt are characteristic of —OH groups. The $\begin{array}{c} \text{—C—OH} \\ \text{//} \\ \text{O} \end{array}$ group is characteristic of

most organic acids, and is known as the carboxyl group.

The members of the homologous series $\text{C}_n\text{H}_{2n+1}\text{COOH}$ are usually known as the saturated fatty acids, since some of the higher members such as palmitic acid $\text{C}_{15}\text{H}_{31}\text{COOH}$ and stearic acid $\text{C}_{17}\text{H}_{35}\text{COOH}$ can be obtained from fats. The first two members, formic and acetic acids, deserve especial mention.

Formic acid H.COOH occurs in the red ant (*formica rufa*), by the distillation of which it was first obtained. It may be prepared by the oxidation of methyl alcohol with chromic acid, or in the form of its salts by the action of carbon dioxide on sodium hydride; also by passing carbon monoxide over soda lime at 210° .



The last method is employed commercially.

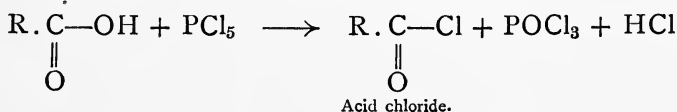
Formic acid furnishes a good example of the well-known fact that the first member of a homologous series often exhibits properties which are almost entirely lacking in any of the other members. Thus while the other fatty acids are remarkably stable substances both in presence of oxidizing agents and of concentrated sulphuric acid, formic acid is a powerful reducing agent. It precipitates many metals from solutions of their salts, *e.g.* silver, mercury, platinum and palladium. The action on a solution of palladious chloride is used for the preparation of palladium black as employed on page 251. Potassium permanganate readily oxidizes it to CO_2 and water. Concentrated sulphuric acid decomposes it

at the ordinary temperature, water and carbon monoxide being produced.

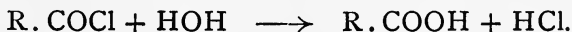
It is important to note that the hydrogen atom directly

linked to carbon in formic acid $\text{H}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$ is not replaceable by a metal, and that the formula of sodium formate is $\text{H} \cdot \overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{ONa}$ and not $\text{Na}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$.

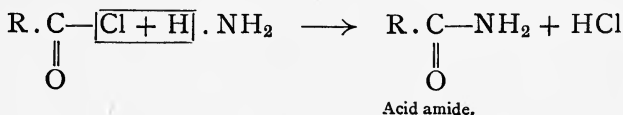
Formyl chloride $\text{H} \cdot \overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{Cl}$ is unknown; all the other acids of this series yield acid chlorides with PCl_5 .



These are colourless liquids, usually possessing an unpleasant pungent odour. They are readily decomposed by water, the acid being regenerated.

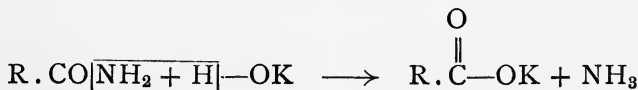


With ammonia they yield acid amides.



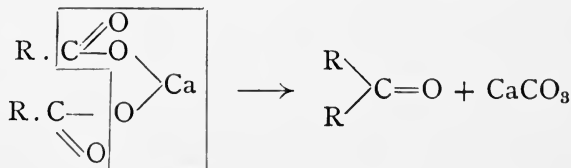
The group $\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$ is known as the acid amide group

and is on no account to be confounded with the amino group $-\text{NH}_2$. The acid amides are usually crystalline solids which on boiling with caustic alkalis are decomposed.



KETONES.

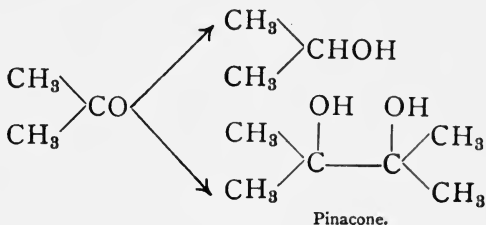
When the calcium salts of the saturated acids $C_nH_{2n+1}COOH$ are submitted to dry distillation the volatile products consist largely of colourless liquids known as ketones, the formation of which is to be represented thus—



Ketones are also obtained by the oxidation of secondary alcohols.



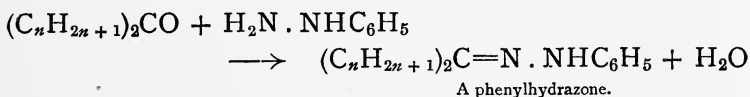
Properties of Ketones.—By reducing agents such as sodium and alcohol or sodium amalgam and water they are reconverted into secondary alcohols. The yield, however, is not always quantitative, since in some cases complex by-products are formed. Thus acetone $\text{CH}_3.\text{CO}.\text{CH}_3$ which may be obtained by the dry distillation of calcium acetate or by the oxidation of isopropyl alcohol, when reduced gives rise not only to isopropyl alcohol but also to a substance known as pinacone.



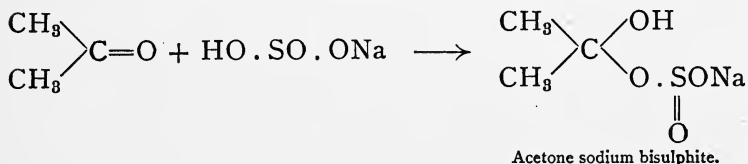
An important property of ketones is the readiness with which they, in common with most aldehydes, which also possess the group ---CO , react with hydroxylamine $\text{H}_2\text{N---OH}$ and phenylhydrazine $\text{C}_6\text{H}_5\text{NH.NH}_2$. Many ketones and aldehydes react also with sodium hydrogen sulphite. With hydroxylamine, oximes are obtained, *e.g.* with acetone.



Phenylhydrazine produces phenylhydrazones thus—

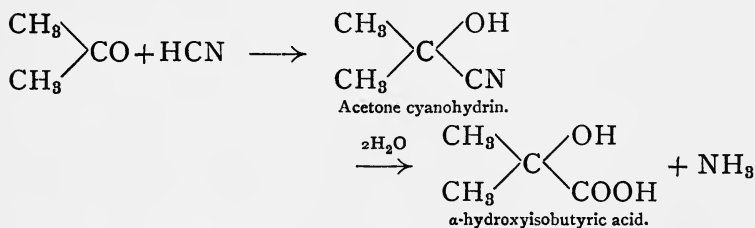


With sodium hydrogen sulphite (usually known as sodium bisulphite) addition products are formed, from which the original ketone may be regenerated by addition of acids.



These so-called bisulphite compounds can therefore be used as a means of purifying ketones and aldehydes, since many of them crystallise well.

Ketones readily combine with anhydrous hydrocyanic acid in presence of a trace of potassium cyanide forming cyanohydrins $\text{R}_2\text{C}(\text{OH})\text{CN}$ which are easily converted into the corresponding hydroxy acids by hydrolysis with concentrated acids, *e.g.*—

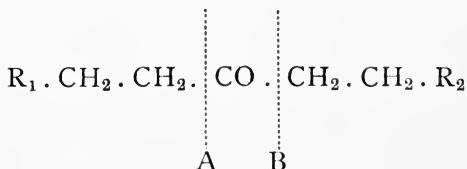


The reaction between aliphatic ketones and ammonia is rather complicated, and leads to the formation of products derived by the elimination of water from one molecule of ammonia and either two or three of acetone. These are known as "Acetoneamines."

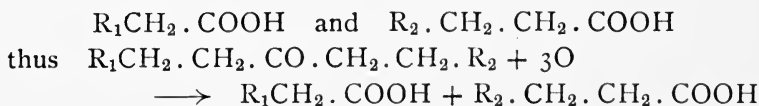
Ketones readily undergo oxidation. The process, however, is not a very simple one. The molecule will be attacked by the oxidizing agent at its weakest point, this

is, of course, the $C=O$ group, since here we have a double linking between the C and the O atoms, which, in its susceptibility towards oxidizing agents, resembles the $C=C$ bond.

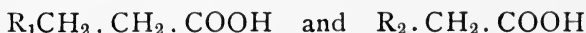
A ketone of the formula $R_1 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot R_2$, where R_1 and R_2 are hydrocarbon residues, may undergo oxidation in two ways, which can be represented thus—



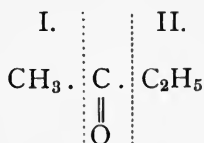
If the molecule be split at the position A, we shall obtain by oxidation the acids—



while if the oxidation occur at the position B, the acids—



Thus if R_1 and R_2 are different radicals, four different acids will be produced; if they be the same, only two acids will be found in the reaction mixture. When methylethylketone



is oxidized, formic acid, $H \cdot COOH$, and propionic acid, $CH_3 \cdot CH_2 \cdot COOH$, will be produced at position I., while if the break occur at II., we shall obtain two molecules of acetic acid, so that three different acids result.

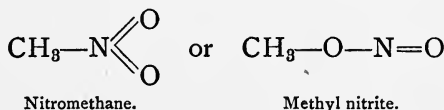
It has been found that, as a rule, that reaction predominates which leaves the carbonyl group in union with the smallest alkyl residue.

NITRO-COMPOUNDS.

The group $\text{—N} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$, which is characteristic of nitric acid,

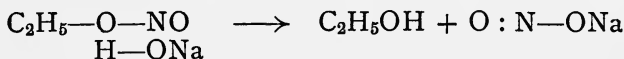
$\text{H—O—N} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$, is known as the nitro-group. It is present in

a large number of organic substances, which are, in consequence, known as nitro-compounds. The nitro-group is carefully to be distinguished from the nitrite group, —O—N : O , which is characteristic of nitrous acid, H—O—N : O . For example, the compound CH_3NO_2 may be either



When ethyl iodide reacts with silver nitrite, two isomeric substances are produced, having the formulæ $\text{C}_2\text{H}_5\text{NO}_2$. The first boils at 17° , and the second at $113^\circ\text{--}114^\circ$. They can, therefore, readily be separated by fractional distillation.

The lower-boiling isomer yields sodium nitrite and ethyl alcohol with caustic soda, and must, therefore, be an ethyl ester of nitrous acid



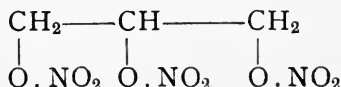
The other isomer does not so react. On the other hand, when reduced with tin and hydrochloric acid, or with sodium amalgam, it yields a compound free from oxygen, and possessing an odour recalling simultaneously that of ammonia and of lobsters. It will be proved in the next section that two hydrogen atoms have replaced two oxygen atoms to form a compound, with the constitution $\text{CH}_3\cdot\text{CH}_2\cdot\text{NH}_2$, known as ethylamine.

The nitro-compounds of the aliphatic series are relatively unimportant. On the other hand, the aromatic nitro-compounds find enormous application in the manufacture of dye-stuffs, and also of explosives.

Certain substances, *e.g.* nitro-glycerol and nitro-cellulose, are incorrectly so called, since they are not nitro-compounds at all, but rather, nitrates. That is to say, the —NO_2 group is

not directly linked to carbon, as in nitroethane or nitrobenzene (page 48), but indirectly through oxygen.

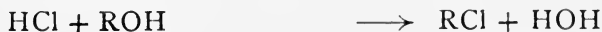
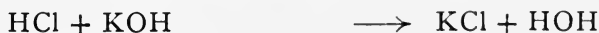
Thus, the so-called nitroglycerin or nitroglycerol has the constitution—



and should be known as glyceryl trinitrate.

ESTERS.

Just as a salt is derived from an acid by replacing the hydrogen by a metal, so an ester is to be regarded as an acid in which the replaceable hydrogen has been substituted by a hydrocarbon radical. If R be an alkyl radical, we may illustrate this by the following analogies:—



An alcohol.

Alkyl chloride or alkyl ester of HCl.



Hydrogen potassium sulphate.



Hydrogen alkyl sulphate.
Alkyl sulphuric acid.



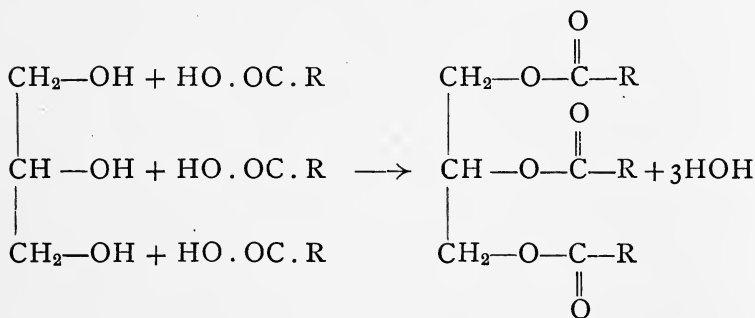
Dialkyl sulphate or dialkyl ester of sulphuric acid.

With an organic acid, *e.g.* acetic acid—



Alkyl ester of acetic acid.

In the case of an alcohol such as glycerol, which is a symmetrical trihydroxypropane, three molecules of a monobasic acid are required to produce the ester.



where $\text{R} = \text{C}_{15}\text{H}_{31}$, we have tripalmitin or glyceryl tripalmitate, a naturally occurring fat. Compare the action of aluminium hydroxide on hydrochloric acid—

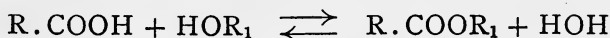


The monoalkyl esters of sulphuric acid are known as alkyl sulphuric acids, and are fairly strong acids. They may also be obtained, see page 212, by the addition of H_2SO_4 to unsaturated hydrocarbons of the ethylene series.

It will be seen from the examples given above that the constitution and method of formation of the esters is analogous to that of the inorganic salts.

Attention must, however, be directed to one important difference. Whereas the formation of salts from an acid and an inorganic hydroxide is practically instantaneous, the formation of an ester by the interaction of an acid and an alcohol usually takes place slowly, and under ordinary conditions is never complete. The velocity of the reaction is much increased if the temperature be raised.

If an ester be treated with water, it undergoes a partial decomposition into acid and alcohol. This reaction, however, like the reverse process of ester formation, does not complete itself, an equilibrium being established between water and ester on the one hand, and acid and alcohol on the other. We may therefore express the formation and decomposition of esters in one equation, which we write thus—



We are dealing with what is known as a balanced action. When the acid and alcohol are heated together a condition

is finally reached in which, at any moment, as much ester is decomposed as is produced, and consequently, neither reaction progresses further. This is what is meant by a state of equilibrium.

By a careful study of the dynamics of the reactions occurring in the system ethyl alcohol-acetic acid—



it has been found that whether reaction take place between one gram molecule of acetic acid and one gram molecule of ethyl alcohol on the one hand, or the equivalent quantities of ethyl acetate and water on the other, the composition of the reaction mixture, when equilibrium is attained, is always the same, namely—

$\frac{1}{3}$ gram molecule ethyl alcohol + $\frac{1}{3}$ gram molecule of acetic acid + $\frac{2}{3}$ gram molecule water + $\frac{2}{3}$ gram molecule ethyl acetate.

That is to say, the position of equilibrium is the same, whether it be approached from the left hand or the right hand of the equation. Similar phenomena accompany the interaction of all acids and alcohols.

Now, it can be proved mathematically, and demonstrated experimentally that the presence of an excess,* either of acid or of alcohol, will tend to shift the position of equilibrium further to the right-hand side of the equation, *i.e.* the yield of ester is augmented. An equivalent excess of either acid or alcohol produces exactly the same effect on the equilibrium position.

Conversely, by addition of excess of water or ester to the reaction mixture the position of equilibrium is moved towards the left of the equation, *i.e.* the yield of ester is diminished. In equivalent quantities the effect of water and ester on the position of equilibrium is the same.

In order to obtain a good yield of ester it is desirable therefore that

- (i) Excess of alcohol or acid be employed.
- (ii) The materials should be absolutely dry.
- (iii) The ester should be removed as fast as it is formed—this may be effected by distillation.
- (iv) The water should be removed by some dehydrating agent such as concentrated sulphuric acid.

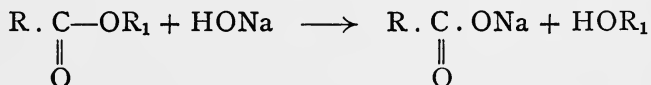
* When excess of alcohol, water, or ester is spoken of, it should be obvious that a quantity greater than that required by the equation is indicated.

In practice all these precautions are combined. See the preparation of ethyl acetate, page 274.

It has been mentioned that the velocity of reaction between an acid and an alcohol is much increased by a rise of temperature. It is important to notice, however, that this hardly affects the position of equilibrium.

If equivalent quantities of alcohol and acetic acid interact at 10° equilibrium is obtained when 65.2 per cent. of the theoretical yield of ester has been obtained, this does not take place, however, for several years; at 220° equilibrium is obtained in 38 hours, and the yield of ethyl acetate is 66.5 per cent. of the theoretical.

Saponification.—If an ester be boiled with caustic alkalis the decomposition proceeds much more rapidly than when water alone is used, and is usually complete in a short time. Mineral acids are also frequently employed in the hydrolysis of esters.



The former process is known as saponification, and the ester is said to be saponified.

One of the earliest examples of this process was the decomposition of fats by means of crude alkalis obtained from wood ashes. The products of the reaction consist of glycerol (trihydroxypropane) and a mixture of the alkali salts of palmitic, stearic and oleic acids, which has ever since been used as soap, whence the derivation of the term saponification.

Soap is still prepared in this way, and it may be mentioned that many naturally occurring oils and fats such as linseed, castor, palm, and cotton-seed oils can also readily be saponified with the production of glycerol and a soap, the acid of which varies, however, with the particular oil employed. These oils should carefully be distinguished from unsaponifiable products such as petroleum and coal tar oils (see Chapter XXI.).

ETHERS.

The homologous series of which the members belong to the class known as aliphatic ethers must now be considered. These substances are produced when an alkyl iodide reacts with the sodium derivative of an alcohol. This synthesis was

discovered by Williamson, and is of very general application. The sodium derivatives of phenols (see page 52) also react with alkyl iodides forming mixed aliphatic aromatic ethers—

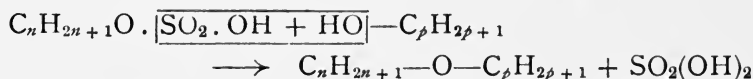
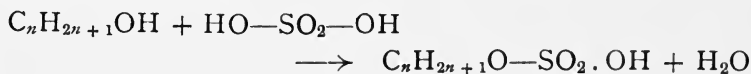


where R_1 may be either an aliphatic or an aromatic radical. Similarly, compounds of the type $R.S.Na$ react with alkyl iodides forming thio-ethers.



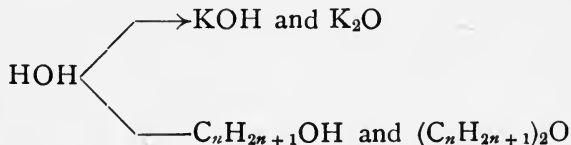
thus indicating the great usefulness of the reaction.

Ethers of the aliphatic series are also obtained by the action of concentrated sulphuric acid on the lower alcohols $C_nH_{2n+1}OH$. An alkyl sulphuric acid is first formed which then reacts with more alcohol regenerating sulphuric acid which can again enter into reaction with a third molecule of alcohol. The formation of water, which dilutes the acid, prevents the sulphuric acid from "etherifying" an indefinite quantity of alcohol.



$C_pH_{2p+1}OH$ the second alcohol molecule may be either the same as or different from the first, the scope of the reaction being therefore considerably extended.

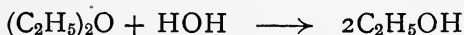
As can be seen from the formulæ, the ethers may be looked upon as water in which each hydrogen atom has been replaced by a hydrocarbon residue. They are therefore analogous in composition to the metallic oxides; we shall see also that some of their reactions are analogous.



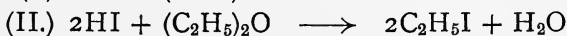
The lower members of the homologous series are very volatile substances (dimethyl ether CH_3-O-CH_3 is a gas at ordinary temperatures) which are characterized by their ready inflammability. For the precautions which are always

to be observed in dealing with the poisonous and dangerously inflammable diethyl ether, commonly known as ether (see page 77).

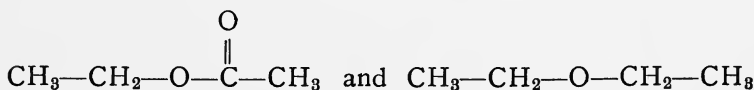
Chemical Properties.—The ethers are relatively very stable substances, especially towards oxidizing agents. On heating with acidulated water at 150° in a sealed tube, alcohol is obtained.



With hydriodic acid at a low temperature two reactions occur—



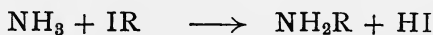
The term “ether” is frequently applied to substances which are not ethers at all. In older text-books and in quasi-scientific literature *esters* are frequently designated as ethers, *e.g.* ethyl acetate is called acetic ether. The incorrectness of this is indicated by a comparison of their formulæ.



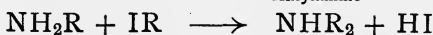
A mixture of low-boiling hydrocarbons of the paraffin series (C_5H_{12} , C_6H_{14} , C_7H_{16}) is sold under the name of petroleum ether, doubtless on account of its great volatility and ready inflammability.

ALIPHATIC AMINES.

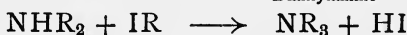
When an alkyl iodide RI is heated with ammonia, the product of the reaction is not homogeneous, but consists of a mixture of four substances produced according to the sub-joined equations.



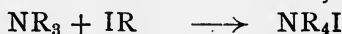
Alkylamine



Dialkylamine



Trialkylamine



Tetra-alkylammonium iodide

It will be seen therefore that the three hydrogen atoms of ammonia may be successively replaced, and that finally a product results which is to be regarded as ammonium iodide in which four hydrogen atoms have been replaced by alkyl groups.

Primary amines are those in which one hydrogen atom of the ammonia has been replaced ; secondary, those in which two alkyl groups are present, whilst in tertiary amines the whole of the hydrogen of the original ammonia has been substituted.

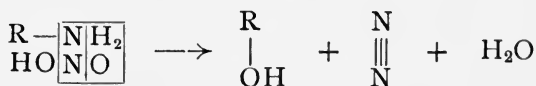
That the product obtained by the reduction of nitroethane possesses the constitution $C_2H_5NH_2$ follows from the fact that it can be obtained by the action of ammonia on ethyl iodide.

In order to separate the products of such a reaction, advantage is taken of the fact that on rendering the mixture alkaline (the various amines being present in the form of their salts with hydriodic acid), and distilling in steam, only the amines pass over, while the tetra-alkylammonium iodide remains behind.

The amines of lower molecular weight may be separated from each other by fractional crystallization of their salts with hydrochloric, hydrobromic, or hydriodic acids. Mixtures containing primary, secondary, and tertiary amines of higher molecular weight may be separated by fractional distillation.

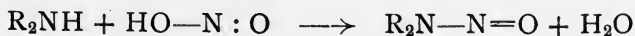
The determination whether a given amine should be classified as a primary, secondary, or tertiary amine is comparatively easy. Nitrous acid may be employed for this purpose.

With primary amines nitrogen is evolved and a primary alcohol formed, the reaction being represented thus—



A similar reaction takes place between primary aromatic amines and nitrous acid, phenols being produced. In this case it is important to note that rather unstable intermediate products, the so-called diazonium compounds, can be isolated. (See page 208.)

With secondary amines, crystalline derivatives known as nitrosoamines are produced—



Tertiary aliphatic amines are usually unattacked by nitrous acid.

Since the amines are derivatives of ammonia, it is not surprising to find that they possess basic properties.

CYCLIC COMPOUNDS.

Under this classification we include those substances of which the molecules possess one or more closed chains of atoms.

If these chains or "rings" contain only carbon atoms, the substance is said to be homocyclic; if, however, in addition to carbon they contain the atoms of other elements such as nitrogen, oxygen or sulphur, the compounds in question are known as heterocyclic compounds.

The most important members of the homocyclic division are those compounds usually classified under the heading, "aromatic series." Many of these compounds occur in various plants and flowers, and possess a pleasant odour, hence the name.

The most important member of the aromatic division of the homocyclic compounds is benzene, and since it may be regarded as the parent substance of all other aromatic hydrocarbons and their derivatives, these substances are frequently known as benzene derivatives in distinction from the aliphatic compounds which are derived from methane.

Benzene C_6H_6 .—If acetylene be passed through a red-hot tube, various aromatic substances are obtained and, among them, benzene. On the other hand, on passing benzene through a heated tube a certain amount of acetylene is produced along with a substance known as diphenyl $C_{12}H_{10}$. The formation of benzene from acetylene is sometimes called a polymerization process, since the original acetylene may be regenerated, though not at ordinary temperatures. (See page 24.)

It is however more correct to regard benzene as a condensation product of acetylene, especially as the union of the acetylene molecules takes place by means of C—C linkages, and the resulting hydrocarbon is very stable.

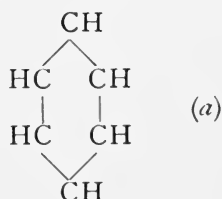
Benzene is found to have a composition represented by the formula C_6H_6 . The corresponding hydrocarbon of the paraffin series, which contains six atoms of carbon has had the formula C_6H_{14} assigned to it as the result of analysis.

It would therefore be reasonable to expect that as benzene

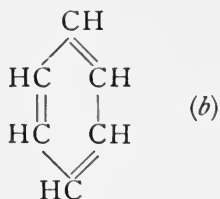
contains eight hydrogen atoms less than hexane, it would exhibit the properties characteristic of unsaturated hydrocarbons.

Such properties it emphatically does not possess, *e.g.* benzene does not add on a molecule of sulphuric acid, nor is it attacked by potassium permanganate or many of the other oxidizing agents. Neither does it form an addition product with the halogens, except in presence of sunlight, when a compound $C_6H_6Cl_6$ is slowly formed; this reaction is entirely different from the instantaneous addition of chlorine or bromine which takes place with unsaturated compounds such as ethylene.

For these and other reasons which cannot fully be entered into here, a cyclic formula has been assigned to benzene—

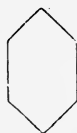


It will be seen at once that all the carbon atoms are represented as trivalent. This we know from experience to be rather unlikely. If the formula originally proposed by Kekulé



be examined it will be seen at once that the valency question now offers no difficulty, but the presence of ethylenic linkages in the molecule would appear to be at variance with the experimental evidence which has just been referred to. A modified form of the Kekulé benzene formula has been proposed by Thiele, which is based on the theory of what is known as Residual Affinity. A discussion of this and other benzene formulæ falls, however, entirely outside the scope of this volume. When writing the formula of benzene,

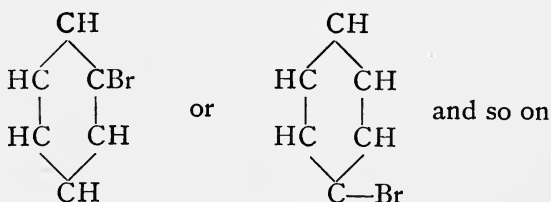
therefore, we shall use exclusively the simple hexagon (a) which can conveniently be simplified to



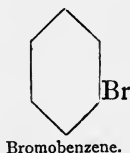
in which the six —CH groups are understood, and the question of the fourth valency of each carbon atom is left out of consideration.

From a consideration of the cyclic formula for benzene it can be readily seen that the six hydrogen atoms are of equal value, since the configuration is symmetrical. If this be so we should expect that monosubstitution products of benzene would not be capable of existing in isomeric forms, *i.e.* that there should be only one monobromobenzene, only one mononitrobenzene, and so on. This conclusion has been verified by experiment.

It is therefore quite immaterial at which corner of the benzene nucleus we write the substituting group in a mono-derivative of benzene, thus bromobenzene may be written—



For convenience the carbon and hydrogen atoms are usually omitted, and the formula written, *e.g.*

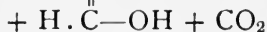
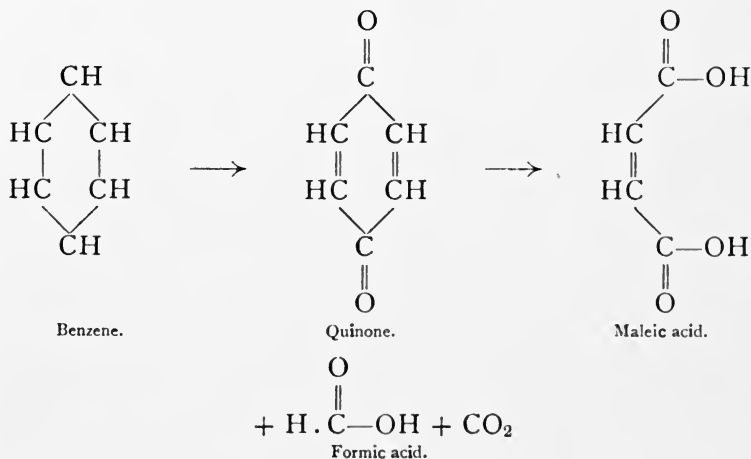


Bromobenzene.

When a hydrogen atom of the nucleus is replaced by another atom or radical, this substituting group is known as the substituent.

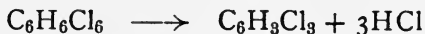
The stability of the benzene ring, which has been already referred to, is further illustrated by its behaviour towards halogen hydrides with which it forms no addition products.

By the action of vigorous oxidizing or reducing agents the benzene ring can be broken. Thus with concentrated hydriodic acid, one of the most powerful reducing agents known, it is converted into hexane C_6H_{14} the well-known member of the series of saturated hydrocarbons C_nH_{2n+2} . By the oxidizing action of ammonium persulphate under the catalytic influence of traces of silver salts, benzene gives rise, first to quinone $C_6H_4O_2$, then to maleic and formic acids and carbon dioxide.



SUBSTITUTION PRODUCTS OF BENZENE.

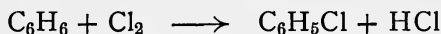
If the hexachloro-addition product of benzene which was mentioned on page 45, be heated, an interesting reaction takes place in which hydrogen chloride and a compound represented by the formula $C_6H_3Cl_3$ are produced. It is therefore to be regarded as benzene in which three hydrogen atoms have been replaced by their equivalent of chlorine.



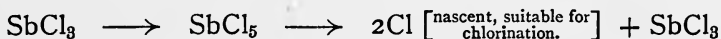
Its constitution is therefore indicated in its rational name which is trichlorobenzene. The prefix chloro always indicates a substitution product, *e.g.* hexachlorobenzene C_6Cl_6 but benzene hexachloride or hexachlorocyclohexane $C_6H_6Cl_6$ is an addition product of benzene.

Although trichlorobenzene is not of much importance, the mono-halogen derivatives of the aromatic hydrocarbons such

as bromobenzene or bromotoluene find considerable application. These are obtained when chlorine or bromine reacts with benzene or its homologues in presence of small quantities of so-called "halogen-carriers" such as sulphur, iron, antimony trichloride, or pyridine. The reaction is to be represented thus—



The halogen carrier probably acts catalytically in that it forms an addition compound with the halogen, *e.g.* SbCl_3 , FeCl_3 , SbCl_5 , $\text{C}_5\text{H}_5\text{NBr}_2$ which can part with some of its halogen to the hydrocarbon, being itself reduced to a compound poorer in chlorine or bromine, which is then immediately reconverted into the higher halogenated product, and so on,



It has been shown that antimony pentachloride in absence of chlorine is capable of chlorinating certain compounds so that the explanation given above is probably correct.

Firmly-fixed Substituents.—A consideration of the properties of the monohalogen substituted benzene hydrocarbons, *e.g.* bromobenzene, chlorotoluene, chloroxylene, and so on, shows very clearly that these compounds differ very considerably in their behaviour from the halogen derivatives of the hydrocarbons $\text{C}_n\text{H}_{2n+2}$ of the fatty series.

It will be remembered that the halogen atoms of the alkyl halides are very reactive, *e.g.* they enter readily into reaction with potassium cyanide, silver nitrite, silver hydroxide, and hydroxides of the alkali metals, silver or other metallic halides being produced. The monohalogen derivatives of the aromatic hydrocarbons react with none of these substances, except in certain cases under high temperatures or pressures. Their halogen atoms may therefore be said to be very firmly fixed.

Although the ring of six carbon atoms present in aromatic hydrocarbons exhibits little tendency to open and give rise to straight chain derivatives, the substitution of the hydrogen atoms of benzene and its homologues is a fairly easy matter. The preparation of nitrobenzene, of which the formation proceeds according to the equation—



is described on page 202.

Similarly, the sulpho group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}-\text{OH} \\ \parallel \\ \text{O} \end{array}$ may be introduced

into the nucleus with comparative ease at 0° when fuming sulphuric acid is employed. With ordinary concentrated sulphuric acid it is necessary to heat the mixture for some hours.

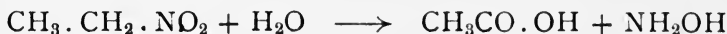


In presence of anhydrous aluminium chloride and oxygen, benzene is partially converted into phenol.



The action of the aluminium chloride is not understood.

The mononitro derivatives of aromatic hydrocarbons resemble the monohalogen compounds in that the $-\text{NO}_2$ group is also very firmly fixed. Thus while nitroethane is converted into acetic acid and hydroxylamine by boiling with hydrochloric acid—

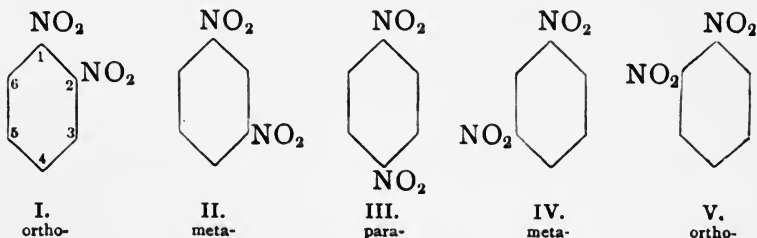


this reagent has no action on the corresponding aromatic compounds, such as nitrobenzene, nitrotoluene, and so on.

Disubstitution Products of Benzene.—It has been established experimentally that disubstituted derivatives of benzene such as dinitrobenzene $\text{C}_6\text{H}_4(\text{NO}_2)_2$ dichlorobenzene

$\text{C}_6\text{H}_4\text{Cl}_2$, bromotoluene, $\text{C}_6\text{H}_4\begin{array}{l} \text{Br} \\ \text{CH}_3 \end{array}$, etc., exist in three and

only three isomeric forms. If we attempt to construct formulæ for all the possible dinitrobenzenes we shall find that some of the configurations are identical, thus—



The first three configurations are clearly different since in the first case the two nitro groups are attached to adjacent carbon atoms, in the second they are separated by one, and in the third case by two carbon atoms. These different configurations represent definite individual compounds.

It will readily be seen, however, that formulæ I. and V. and II. and IV. are identical, so that the number of different formulæ which can be written is reduced to three.

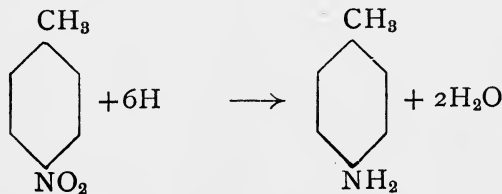
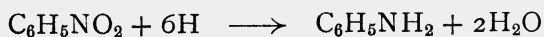
Two substituents in the 1:2 relation to each other are said to be in the ortho-position, and the compound is called an ortho-compound; the 1:3 relation is known as the meta-position, while the 1:4 relation is designated the para-position.

It is, of course, immaterial which of the carbon atoms of the benzene nucleus shall have the number one assigned to it; nevertheless, it is customary to designate the top carbon atom of the hexagon as 1, and to number the others in the direction of the motion of the hands of a clock.

AROMATIC AMINES.

As in the aliphatic series, we meet with primary, secondary and tertiary amines. Some of these are high-boiling liquids, but many secondary and tertiary amines are solids. They are all only sparingly soluble in water.

The primary amines may be prepared by the reduction of the corresponding nitro-compounds by means of nascent hydrogen. Thus nitrobenzene yields aniline, *p*-nitrotoluene yields *p*-toluidine.



Owing to the non-reactivity of the mono-substituted halogen derivatives of the aromatic hydrocarbons (see page 48), it is not possible under normal conditions to obtain aromatic amines by the interaction of ammonia and these substances. If, however, monochlorobenzene be heated in an autoclave to 200° with a concentrated aqueous solution of ammonia in

presence of a small amount of copper sulphate, a fairly good yield of aniline is obtained.

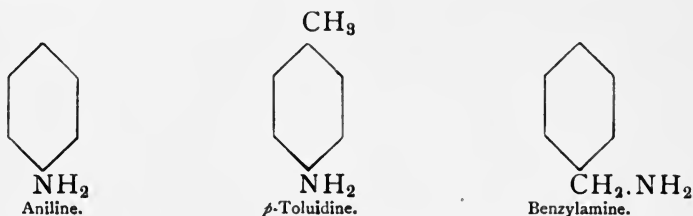
In spite of this reaction, which is probably due to catalysis, the difference in the behaviour of aliphatic and aromatic halogen compounds is sufficiently striking.

The behaviour of the primary aromatic amines towards nitrous acid is described on page 208. They are weaker bases than the primary aliphatic amines. This is to be attributed to the diminution in the basic properties of ammonia resulting from the introduction into the molecule of the acidic or negative phenyl group, C_6H_5- .

Nevertheless, the primary aliphatic amines combine with acids to form well crystallized soluble salts, thus—



It is worthy of note that the ammoniacal odour so characteristic of the aliphatic amines is completely absent in those derivatives of benzene containing an amino group directly linked to a carbon atom of the nucleus. On the other hand, compounds such as benzylamine, in which the $-NH_2$ is not so attached, but is separated by an intervening carbon atom, possess more of the properties of the aliphatic amines, *e.g.* ammoniacal odour and strong alkalinity. Moreover, they absorb carbon dioxide like the corresponding aliphatic compounds.



Secondary Aromatic Amines.—These may be obtained by heating a mixture of an aromatic amine and its hydrochloride, thus—



Diphenylamine $(C_6H_5)_2NH$ may be obtained in this way from aniline.

The mixed fatty-aromatic secondary amines may be

* Ar = phenyl C_6H_5 , tolyl $C_6H_4 \cdot CH_3$, etc.

obtained by the interaction of an alkyl iodide with a primary aromatic amine—



In this case, as with ammonia and an alkyl iodide, a certain amount of $(\text{C}_6\text{H}_5)(\text{C}_n\text{H}_{2n+1})_2\text{N}$ and $(\text{C}_6\text{H}_5)(\text{C}_n\text{H}_{2n+1})_3\text{NI}$ would be formed.

The secondary aromatic amines are less basic than the primary, due obviously to the introduction of another negative or acidic phenyl group into the molecule. Their salts with strong acids are partially hydrolyzed on addition of water.

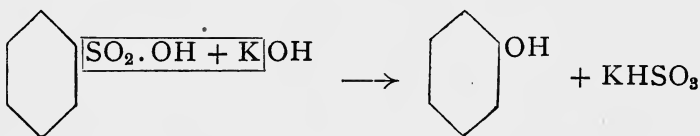
The tertiary amines NAr_3 have been but little investigated. They have practically no basic properties.

PHENOLS.

The hydroxyl derivatives of the aromatic hydrocarbons are known as phenols, which are designated mono-, di-, or trihydric, according to the number of hydroxyl —OH groups which are directly attached to carbon atoms of the nucleus. In this book we shall deal almost exclusively with the monohydric phenols.

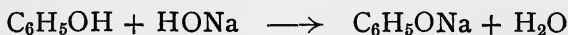
These are usually pleasant-smelling liquids or low-melting solids, many of which possess strongly antiseptic properties.

The preparation of monohydroxybenzene $\text{C}_6\text{H}_5\text{.OH}$ by a method which is generally applicable for the conversion of aromatic amines into phenols is described on page 207. The fusion of an aromatic sulphonic acid with potassium hydroxide also gives rise to phenols, *e.g.*—



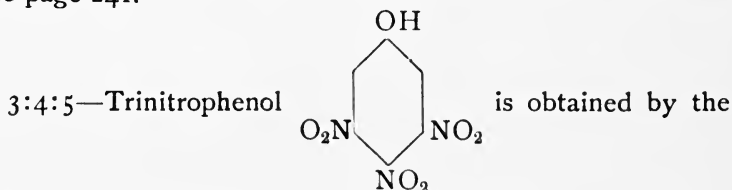
Similarly, disulphonic acids, *e.g.* $\text{C}_6\text{H}_4(\text{SO}_2\text{OH})_2$ on fusion with potash yield dihydric phenols as $\text{C}_6\text{H}_4(\text{OH})_2$.

The monohydric phenols have acidic properties and dissolve in caustic alkalies forming phenoxides (compare the formation of alkyl oxides from sodium and aliphatic alcohols).



They are not, however, sufficiently strongly acid to liberate CO_2 from carbonates, although compounds such as nitrophenol $\text{C}_6\text{H}_4\begin{matrix} \text{OH} \\ \text{NO}_2 \end{matrix}$, in which the acidity of the molecule is much increased by the entry of the $-\text{NO}_2$ group, do so readily.

For other properties of phenol, see page 207. For its extraction from coal tar, in which it occurs to a large extent, see page 241.

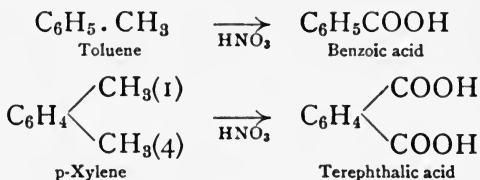


action of strong sulphuric acid and fuming nitric acid on phenol. It is known as picric acid, and is a strong dye-stuff. It is largely used in the manufacture of explosives.

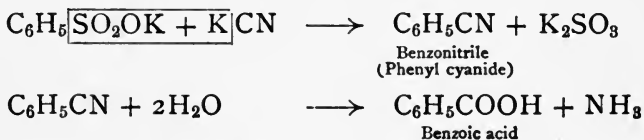
THE ACIDS OF THE BENZENE HYDROCARBONS.

These have the general formula $\text{C}_n\text{H}_{2n-7}\text{COOH}$, and may be prepared

(i) By oxidation of certain hydrocarbons, *e.g.*—

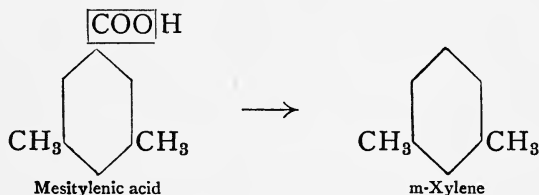


(ii) From the potassium salts of sulphonic acids by conversion into cyanides and subsequent boiling with hydrochloric acid.



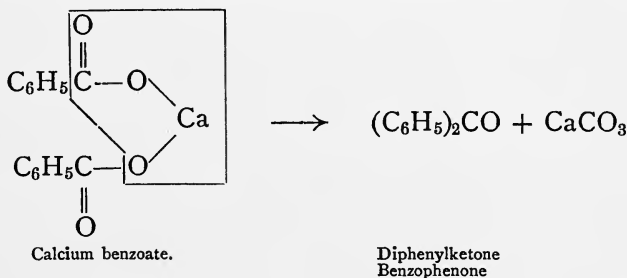
On distillation with soda lime, all aromatic carboxylic

acids* are converted into aromatic hydrocarbons or their substituted derivatives.



(Compare preparation of C_6H_6 , page 201.)

On distillation of their calcium salts, aromatic ketones are formed with properties resembling the ketones of the aliphatic series, except that they are usually solids.



For a description of the aromatic aldehydes and ethers a text-book of pure organic chemistry should be consulted.

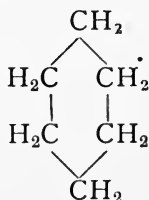
POLYMETHYLENES.

It has already been mentioned that benzene, when heated with concentrated hydriodic acid is converted into normal hexane C_6H_{14} , eight hydrogen atoms being taken up and the ring broken.

If, however, benzene vapour mixed with hydrogen be passed through a heated tube containing freshly reduced nickel only six hydrogen atoms enter into combination, and a liquid having the composition C_6H_{12} and known as hexamethylene, hexahydrobenzene or cyclohexane is obtained. Since this is a perfectly saturated substance and yet contains two hydrogen atoms less than normal hexane its constitution must be represented by a ring of six carbon atoms, each

* A carboxylic acid is one which contains the carboxyl group —C—OH .
 \parallel
 O

linked to two atoms of hydrogen. Its formation from benzene in the manner just described is further and conclusive evidence in this direction



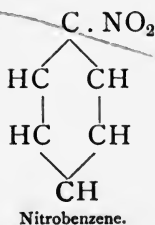
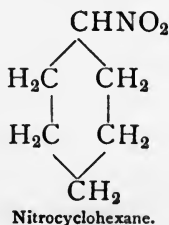
Cyclohexane boils at 80° , while benzene boils at 80.4° , so the removal of any unchanged benzene from the product of the reaction must obviously be effected by methods other than fractional distillation.

The process usually adopted is to test the well-cooled mixture, which usually contains only small amounts of benzene, with cold fuming sulphuric acid. This immediately sulphonates the benzene, forming benzenesulphonic acid $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{OH}$, while the cyclohexane is unchanged and can be separated mechanically, washed, dried and distilled. This method of procedure is well adapted to the preparation of the homologues of cyclohexane, *i.e.* the hexahydro derivatives of the other aromatic hydrocarbons, *e.g.* toluene yields methylcyclohexane, and any which remains unchanged is converted into the isomeric toluenemonosulphonic acids (see page 254).

Cyclohexane and its homologues are known as *naphthenes* and occur to a large extent in Caucasian petroleum.

Concentrated nitric acid or a mixture of concentrated nitric and sulphuric acids is practically without action on the hexahydroaromatic hydrocarbons in the cold. Nevertheless hot strong nitric acid gives rise to nitrobenzene, the reaction being therefore, first an oxidation and then a nitration.

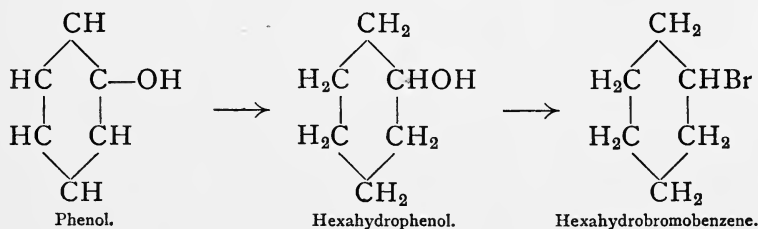
On the other hand, nitro compounds of the hydroaromatic hydrocarbons can be prepared by heating the latter with dilute nitric acid in a sealed tube. Nitrocyclohexane $\text{C}_6\text{H}_{11}\text{NO}_2$ smells like nitrobenzene and boils at 206° .



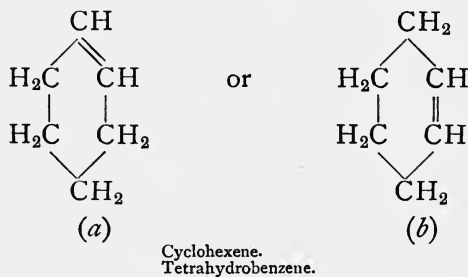
By the action of chlorine on cyclohexane in direct sunlight explosion occurs. Monochlorocyclohexane $C_6H_{11}Cl$ can be isolated from the reaction mixture.

The monohalogen derivatives of cyclohexane and its homologues are best prepared, however, by the action of phosphorus trihalides on the corresponding monohydroxy derivatives, the so-called cyclohexanols.

Cyclohexanol and some of its homologues can be prepared by the catalytic hydrogenation of phenols in presence of nickel. Thus—



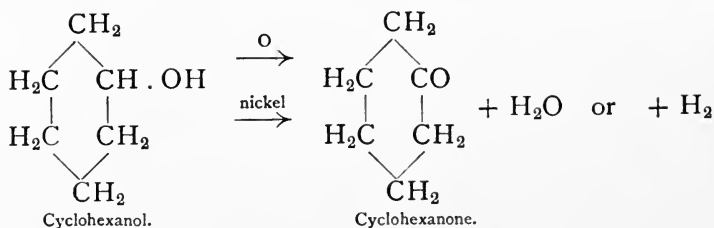
Cyclohexanol or hexahydrophenol is a thick, colourless liquid which has only a very faint phenolic odour, and boils at 160.5° . Dehydrating agents cause the elimination of the hydroxyl group as water and the formation of an unsaturated hydrocarbon C_6H_{10} known as cyclohexene. The homologues of cyclohexanol, *e.g.* hexahydrocresol behave similarly—



Configurations (a) and (b) are, of course, identical.

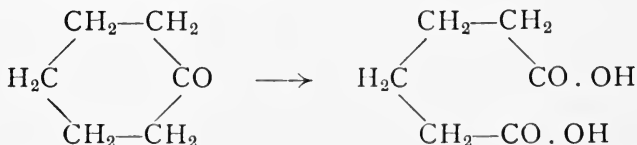
On oxidation with chromic acid the $-\text{CHOH}$ group of cyclohexanol is converted into $-\text{CO}$ and a pleasant-smelling liquid known as ketohexamethylene or cyclohexanone is obtained.

The termination -one is employed in order to indicate the ketonic nature of the substance.

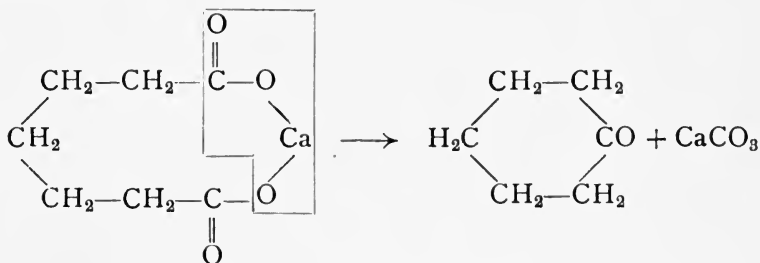


Cyclohexanone is also produced to a certain extent during the catalytic hydrogenation of phenol owing to the dehydrogenating action which is simultaneously exerted by the nickel.

On further oxidation the ring is broken and cyclohexanone is converted into adipic acid



Its homologues, such as methylcyclohexanone, of which there are obviously three isomers, according to the relative positions of the =CO and CH_3- groups, behave similarly on oxidation, alkyl-substituted dibasic acids being obtained. It is very important to note that when the calcium salt of pimelic acid, which is the next higher homologue of adipic acid, is submitted to dry distillation cyclohexanone is produced—



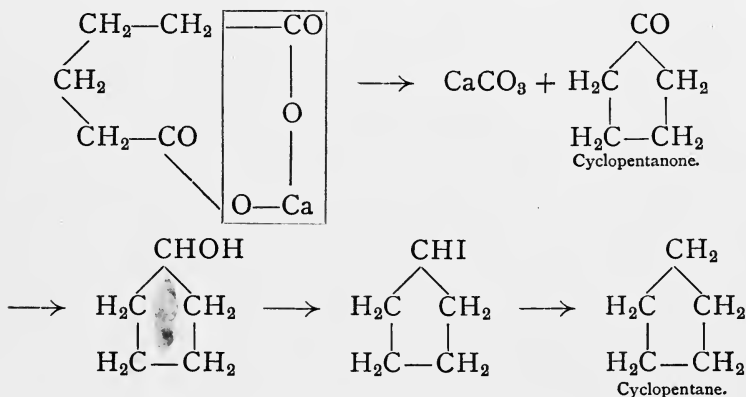
As we shall see later, a similar reaction occurs with various homologues of pimelic acid.

Other Members and Derivatives of the Hydroaromatic, Polymethylene, or Naphthene Class of Hydrocarbons.—The lower

members of the series are mostly of no particular commercial importance though they are full of interest to the research chemist. Some of them, however, occur in Caucasian and to a less extent in American petroleum, *e.g.* cyclopentane C_5H_{10} which boils at 50° .

Cyclopentane has been synthesized in an interesting manner from adipic acid, $COOH.(CH_2)_4.COOH$. When its calcium salt is submitted to dry distillation, calcium carbonate and a ketopentamethylene, known as cyclopentanone and occurring to a small extent in crude wood spirit, are produced.

Cyclopentanone can be reduced by means of sodium and moist ether to cyclopentanol, which with hydriodic acid first forms cyclopentyl iodide (iodocyclopentane) and then cyclopentane. Thus—

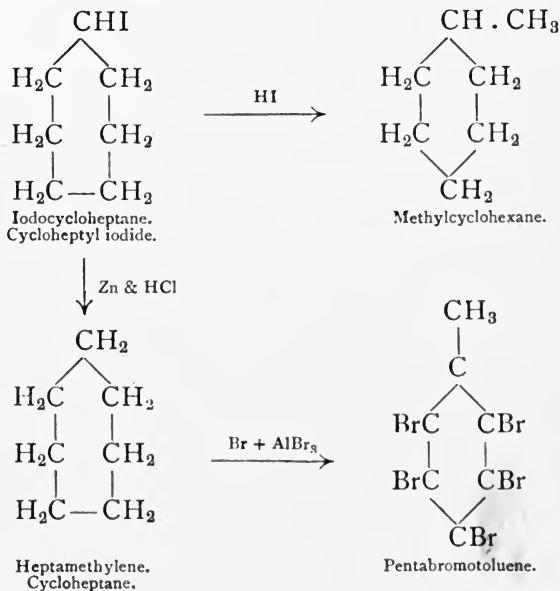


We thus see that the dry distillation of the calcium salt of an aliphatic dibasic acid is an extremely valuable and important reaction.

In complete analogy with the foregoing reactions cycloheptanone, suberone or monoketoheptamethylene can be obtained from the calcium salt of suberic acid, the dibasic acid containing eight atoms of carbon.

This ketone can be reduced to the corresponding cycloheptanol which yields an iodide which on treatment with zinc and hydrochloric acid is converted into heptamethylene. Hydriodic acid cannot be used for this last step since it gives rise to an exceedingly interesting transformation which has many parallels among the hydroaromatic series. Anhydrous hydrogen iodide at 250° converts cycloheptyl iodide not into cycloheptane but into its isomer, methyl cyclohexane, an

instance of the conversion of a seven carbon ring into one containing only six atoms of that element. Dimethylpentamethylene is also produced in the same reaction. Similarly, cycloheptane (also known as suberane, to be carefully distinguished from suberone) is converted by bromine in presence of anhydrous aluminium bromide into pentabromotoluene which is, of course, a derivative of the six carbon atom ring, benzene—

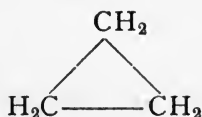


Cycloheptane is a liquid possessing an odour resembling that of petroleum-naphtha and boiling at 117° under 736 mm. pressure.

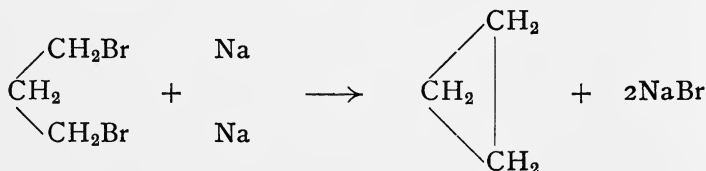
Octomethylene C_8H_{18} has recently been prepared by a very complicated process. It melts at 11° .

Nonomethylene C_9H_{18} is a liquid of boiling-point $170-172^\circ$, and is prepared by methods exactly similar to those employed in the syntheses of penta- and heptamethylene. The starting point was the calcium salt of sebacic acid $\text{COOH} \cdot (\text{CH}_2)_8 \cdot \text{COOH}$.

Cyclopropane or Trimethylene C_3H_6 is a gas which possesses a constitution represented by the formula—



It may be prepared by the action of sodium on trimethylene bromide $\text{BrCH}_2\text{—CH}_2\text{—CH}_2\text{Br}$ a compound which is best prepared from glycerol $\text{HOCH}_2\text{—CHOH—CH}_2\text{OH}$ by a rather complicated process—

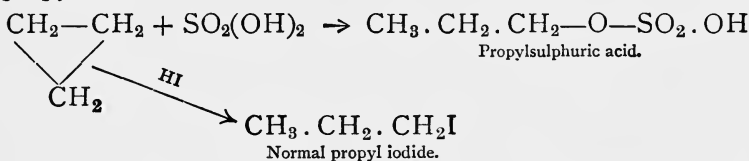


The action of sodium on homologues of trimethylene bromide in which the bromine atoms are separated by a larger number of methylene groups is a method of general application in the synthesis of naphthene hydrocarbons.

Trimethylene exhibits rather interesting properties. It does not reduce potassium permanganate except on long standing, but it combines with two atoms of bromine. This is, however, not a simple addition reaction. The cyclopropane ring is first broken and *then* two atoms of bromine are taken up and trimethylene bromide produced.

Similarly, concentrated sulphuric acid is capable of breaking the ring, the monopropylester of sulphuric acid or propylsulphuric acid being formed.

Fuming hydriodic acid converts trimethylene into normal propyl iodide.



It would thus appear that a ring containing three carbon atoms is unstable and readily breaks up under the influence of reagents giving rise to straight chain compounds.

Cyclobutane, containing a ring of four carbon atoms, is also unstable though probably to a less extent than trimethylene.

On the other hand, cyclopentane and cyclohexane contain comparatively stable ring systems, as is indicated by the fact that cyclohexane gives rise to ring substitution products with chlorine and the other halogens.

The facts just mentioned are illustrative of a great general principle, namely, that of all homocyclic carbon rings those containing five and six carbon atoms are the most stable,

either a diminution or an increase in the number of carbon atoms resulting in a weakening of the stability of the ring.

POLYMETHYLENE OR NAPHTHENE HYDROCARBONS.

Name.	Formula.	Boiling-point °C.	Specific gravity at 0°.
Trimethylene	C_3H_6	- 35	—
Tetramethylene	C_4H_8	+ 12	0·709
Pentamethylene	C_5H_{10}	49	0·769
Hexamethylene	C_6H_{12}	81	0·799
Methyl pentamethylene . .	C_6H_{12}	72	0·766
Heptamethylene	C_7H_{14}	117	0·830
Dimethyl pentamethylene . .	C_7H_{14}	91	0·778
Methyl hexamethylene . . .	C_7H_{14}	98	0·778
Octomethylene	C_8H_{16}	146	0·856
Dimethyl hexamethylene . .	C_8H_{16}	118	0·781
Nonomethylene	C_9H_{18}	171	—
Trimethyl hexamethylene . .	C_9H_{18}	148	0·787

CHAPTER II

PETROLEUM

ALTHOUGH petroleum is extremely widely distributed, there are only three great oil fields of outstanding importance, namely, those in Pennsylvania, Caucasia, and Galicia.

It has been definitely established that the petroleum from each of these sources is principally composed of the same classes of hydrocarbons, namely aliphatic, aromatic, and hydroaromatic or naphthene, nevertheless the relative amounts of each class vary considerably with the district of origin of the oil.

Thus Pennsylvanian petroleum, although consisting principally of saturated hydrocarbons of the series C_nH_{2n+2} , also contains a certain amount of hydroaromatic and aromatic hydrocarbons. On the other hand, these hydroaromatic or naphthene hydrocarbons predominate very largely in Caucasian petroleum, although members of the other two classes are also present.

When an oil well is first opened, both oil and gas usually issue from the bore hole. In the case of American petroleum the oil contains dissolved solid hydrocarbons. These are sometimes present in such quantities as to be deposited and finally to choke up the bore hole. Again, the mud which collects on the bottom of storage tanks containing crude American petroleum consists largely of solid hydrocarbons. The crude oil of Upper Burmah often contains from 10 to 12 per cent. of these compounds.

Pennsylvanian Petroleum.— We will now consider the chemical nature of the constituents of crude Pennsylvanian petroleum and of "natural gas," afterwards proceeding to a similar treatment of the other crude petroleums. Certain constituents which occur only to a very small extent, will also be dealt with.

As has already been mentioned, Pennsylvanian petroleum consists principally of saturated hydrocarbons of the paraffin series: indeed, with one exception, all the members from methane to pentatriacontane, which boils at 380° – 384° at 50 mm., have been isolated either from the gas or from the

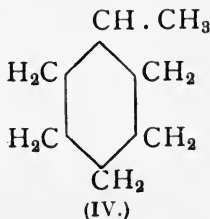
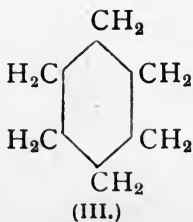
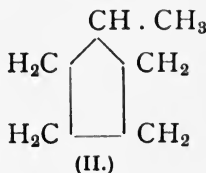
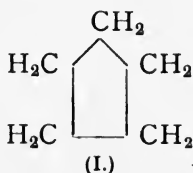
oil. (A list of the more important members of the paraffin series is given in Chapter I., page 9.)

Very frequently several or all of the various structural isomers of a given hydrocarbon are present.

The lower members of the olefine series also occur in the gas and oil from Pennsylvanian wells, ethylene C_2H_4 , propylene C_3H_6 , butylene C_4H_8 , amylene C_5H_{10} and hexylene C_6H_{12} have been isolated, while in Redwood's "Treatise on Petroleum," 1913, vol. i. p. 246, a list of several of the higher members of the olefine C_nH_{2n} series, which are said to occur in North American petroleum, is given, including such compounds as nonylene C_9H_{18} and melene $C_{30}H_{60}$. It is fairly certain, however, that many of the olefine hydrocarbons which occur in purified specimens of petroleum, have been formed during the processes of fractional distillation to which the product has been submitted, and were not originally present in the oil. Nevertheless, varying amounts of olefine hydrocarbons are present in most specimens of crude oil, that from Burmah, commonly known as Rangoon oil, being particularly rich in these compounds.

Certain aromatic hydrocarbons, such as benzene, toluene, xylene, pseudocumene, and mesitylene occur to a small extent in Pennsylvanian oil, whilst Ohio oil contains a rather higher percentage of the homologues of benzene. Naphthalene can be obtained from the fractions of Californian oil, which boil at 220° – 222° .

Several hydrocarbons of the polymethylene series were also obtained in a pure state by Young, from the low-boiling fractions of American petroleum. These are cyclopentane (I.), methylcyclopentane (II.), cyclohexane (III.), and methylcyclohexane (IV.). A dimethylcyclopentane was also obtained.



The same specimens of Pennsylvanian petroleum were found by Young to contain in addition, certain high-boiling hydrocarbons containing 21 to 26 atoms of carbon to the molecule. These, Young considered, belong to the naphthene series, as they are not unsaturated compounds. It is probable that they contain several ring systems. Associated with them are the high-boiling solid paraffins. These can be removed by cooling the mixture and filtering, when the paraffins solidify, but the naphthenes, although containing almost the same number of carbon atoms in the molecule, remain liquid.

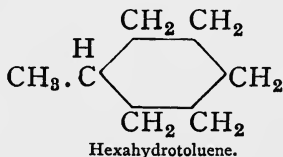
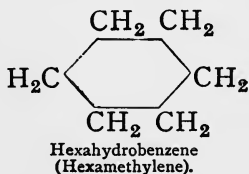
It has been found that acetaldehyde occurs in the crude oils of Pennsylvania and Ohio to the extent of about 0.001 per cent.

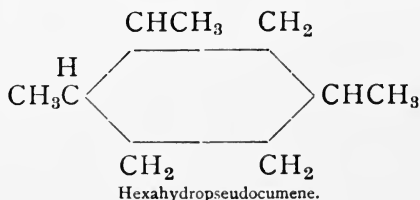
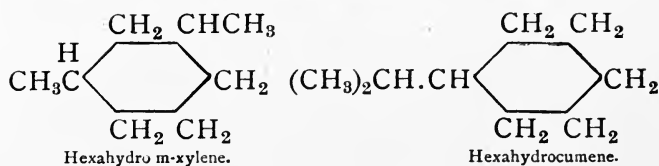
American Natural Gas.—In addition to methane, ethane, and propane this contains certain members of the olefine series. The amount of carbon dioxide which may be present varies considerably and may rise to 10 per cent. or more in some natural gases. Small quantities of carbon monoxide, nitrogen, hydrogen, and oxygen have been detected. Sulphuretted hydrogen is often present in quantities up to about 0.2 per cent.

From analyses carried out on natural gas collected in pipes from a wide area by the Alleghany Heating Co., it would appear that in six years (1886–1892) the average composition of the gas remained unchanged. At times, however, the odour of the higher paraffins became more noticeable than at others.

Caucasian Petroleum consists principally of hydrocarbons of the naphthene or polymethylene class, which have already been mentioned as occurring to a much smaller extent in American petroleum.

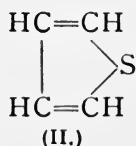
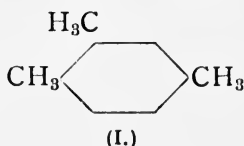
The polymethylene hydrocarbons indicated below have, among others, been isolated from Caucasian petroleum.





The presence of small quantities of hydrocarbons of the acetylene series $\text{C}_n\text{H}_{2n-2}$ was reported by Markownikoff and Mendeléef in the oil of Baku.

The aromatic hydrocarbon pseudocumene (I.)—



occurs in Caucasian petroleum, while thiophen (II.) has been discovered in the oil of Grozni (Caucasus) to the extent of one part per million.

The oil of Tiflis is stated to be largely composed of saturated aliphatic hydrocarbons. This for a Caucasian oil is rather unusual. Pentane C_5H_{12} , hexane C_6H_{14} , and heptane C_7H_{16} , have been isolated from this oil. Di-isopropyl or tetramethyl ethane $(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{CH} \cdot (\text{CH}_3)_2$ has been found in the lower boiling fractions from Baku oil. One of the most characteristic properties of Caucasian petroleum is the almost complete absence therefrom of the high-boiling solid hydrocarbons of the series $\text{C}_n\text{H}_{2n+2}$, which are collectively known as paraffin wax. The quantity of these hydrocarbons is usually less than one per cent.

The "natural gas" arising from the Baku oil wells contains considerable amounts of olefines, in which compounds it is richer than the Pennsylvanian gas.

In common with many oils such as those of Galicia, Roumania and Germany, the Caucasian oils contain a certain amount of free acids; for example, it was found that a fraction of Caucasian petroleum boiling between 220° and 230° contained

5.25 per cent. of oxygen. Some of this was possibly due to the presence of phenols which frequently occur in the Baku oil, but the majority of the oxygen was in the form of acids. As to the nature of these acids there has been some dispute. Probably they are carboxyl derivatives of naphthene hydrocarbons; one of them has, in fact, been converted into octonaphthene by loss of carbon dioxide.

Formic and acetic acids, $\text{H}.\text{COOH}$ and $\text{CH}_3.\text{COOH}$, have been obtained in small amounts from the petroleum of Grozni. Refined Baku oil has been shown to be capable of absorbing atmospheric oxygen, an increase in acidity and a darkening in colour occurring simultaneously.

The Galician oils occupy a position intermediate between those of Baku and of Pennsylvania as regards the proportion of polymethylenes (naphthenes) which they contain.

Several saturated aliphatic hydrocarbons can, however, be isolated from Galician oil, *e.g.* *n*-pentane C_5H_{12} , *n*-hexane C_6H_{14} , *n*-heptane C_7H_{16} , *n*-nonane C_9H_{20} , and *n*-decane $\text{C}_{10}\text{H}_{22}$, as well as some of their structural isomers, *e.g.* iso-pentane $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_3$.

Many of these oils are very rich in paraffin wax, whilst *p*-xylene and pseudocumene are also present in addition to benzene and toluene, which occur to a small extent in practically all oils whatever be the country of their origin.

Certain phenols also occur in the denser oils.

Fractionation of the Crude Oils.—A description of the various forms of stills, fractionating columns, and condensers which are employed in the distillation of crude petroleum need not be given here, since the matter is fully dealt with in textbooks concerned with the strictly technological side of the industry. The preliminary distillation of the crude oil results in its separation into three main fractions. (I) B.P. up to 150° , sp. gr. 0.75–0.77. This is used as a motor spirit and for dry cleaning purposes. (II) B.P. 150° – 300° , sp. gr. 0.87. This forms illuminating oil, the so-called paraffin oil or kerosene. (III) A residue in the still consisting of products boiling above 300° .

The first two fractions are then separately redistilled in order to remove as much as possible of the tarry and resinous matter with which the crude oil is usually contaminated.

After purification in the manner just described, the fraction B.P. up to 150° is carefully fractionated, using an apparatus somewhat similar to that employed in the rectification of alcohol. Great care must be taken during the distillation of

this very inflammable liquid, and in consequence the heating is carried out by means of steam pipes.

At the commencement of the distillation a considerable amount of gas is evolved which consists of ethane, propane, and butane. By the action of cold and pressure, a portion of these gases can be liquefied. A colourless liquid which boils at 0° and has a specific gravity of 0.59 results and is employed in refrigerators on account of the cold produced by its evaporation. It is known as *Cymogene* and consists principally of butane, which in the pure state boils at 1°C .

After removal of the gases an extremely volatile liquid known as *Rhigolene* distils. Unless a freezing mixture such as ice and salt be employed it will probably escape condensation, since it boils at 18°C . It has a specific gravity of 0.62, consists principally of pentane C_5H_{12} , and is employed as a local anæsthetic.

The pure hydrocarbon pentane, which may readily be obtained from rhigolene, is used in the Harcourt Standard lamp for the production of a flame of uniform luminosity. In most European countries except the German and Austrian Empires, this flame is accepted as the standard with which all other sources of illumination are compared. For a description of this and other standard lamps the reader is referred to text-books dealing with photometry.

As the distillation continues, in the neighbourhood of 60° another rather large fraction distils. This consists principally of hexane C_6H_{14} , and is largely used as a solvent for india-rubber.

The second fraction, which distils between 70° and 120° , is commercially known as *Benzine*, and has a specific gravity of 0.70 to 0.72. This mixture of hydrocarbons is largely used as a motor spirit and for the dry cleaning of clothes.

This "Benzine" is frequently submitted to a further distillation, and is separated into two fractions, of which the lighter (*i.e.* the one possessing the lower boiling-point), is known as *benzoline*, and consists principally of heptane, whilst the heavier is designated as *naphtha*. Both these fractions, however, find almost identical uses, and the names which denote them are often loosely employed. "*Petroleum naphtha*" must carefully be distinguished from "*solvent naphtha*," which is a mixture of aromatic hydrocarbons (see page 230). The terms *light petroleum*, *petroleum ether*, and *Sherwood oil* are often used to denote fractions distilling from 70° to 100° or even from 50° to 100° .

The third fraction obtained on redistillation of the original

distillate [B.P. up to 150°] is known as *Ligroin* or *heavy benzine*, comes over from 120° to 135° , and has a specific gravity of 0.73. From 135° to 150° or 160° a fourth fraction is obtained, which is often designated *Polishing Oil*. This contains, of course, all the most difficultly volatile matter which originally distilled below 150° , and possesses the specific gravity 0.74 to 0.77.

This process of redistillation is, however, followed by a further purification, the oil being treated first of all with concentrated sulphuric acid. By this means unsaturated hydrocarbons are converted into esters, which are soluble in sulphuric acid (see page 212), and basic substances are converted into salts; many sulphur compounds are also removed by this operation.

The oil is next shaken with caustic alkali. This neutralizes any sulphuric acid which has not been previously mechanically removed, and also dissolves any acidic constituents of the oil (see page 66). In many cases a final purification by means of litharge, PbO , is resorted to in order to remove easily decomposed sulphur compounds.

In certain cases the oils are filtered and bleached. These operations are frequently applied to each separate fraction collected as above.

We can now consider that portion of the original distillate boiling from 150° to 300° . This, when purified, is used as illuminating oil, and in America is commonly known as *Kerosene*, and in Great Britain as *Paraffin Oil* or *Lamp Oil*.

The purification process consists, as in the case of the lighter distillates, in successive treatment with sulphuric acid, 66 per cent. strength, water and caustic soda solution, the liquids being thoroughly mixed by a stream of compressed air.

If the fractionation be carried out under the conditions which prevail in an ordinary distillation it will be found that a typical Pennsylvanian crude petroleum will yield about 35–50 per cent. of oil suitable for illuminating purposes, and about 20–30 per cent. of lubricating oils.

About 1865, however, it was observed that if the comparatively heavy vapours evolved during the separation of the illuminating oils from the higher boiling portions were allowed to condense and drop back into the still, a much higher yield of kerosene (B.P. 150° – 300°) was obtained, while the quantity of oil suitable for lubricating purposes was diminished. This observation forms the basis of all the so-called “cracking” operations (see Chapter XII.).

At the present time the return of the condensed vapour

to the still is facilitated as much as possible, with the result that in a combined "distillation-cracking" process about 75-80 per cent. of the oil can be used for illumination, but only 6 per cent. as a lubricant.

When, in the distillation of a crude petroleum, the fractions boiling below 150° and between 150° and 300° have been removed, the liquid remaining in the distillation vessel is known as Still Residuum. In the case of Pennsylvanian petroleum this residue represents about 10-25 per cent. of the original crude oil. It is frequently used, without any further treatment, as fuel.

Certain very valuable products contained in this Still Residuum, however, are usually extracted therefrom. We refer principally to lubricating oils and paraffin wax; pitch can also be obtained in large quantities.

Any further distillation of this residue must obviously be carried out in vacuo, otherwise decomposition of the high-boiling hydrocarbons, technically though incorrectly termed "dissociation," will occur. All "cracking" processes are based on this instability of hydrocarbons at high temperatures (see page 193).

Sometimes superheated steam is introduced into the vacuum still in order to accelerate the removal of the volatile constituents. The tendency to decomposition which always exists if the vapours remain long in contact with the surface of the still, which is heated by direct firing, is thereby diminished. The portion which first distils forms about 20-25 per cent. of the total residuum. This is used either as a burning oil or later on returned to the still along with a fresh charge of residuum. The next portion of the distillate, which contains much paraffin wax, is agitated while still hot with about 4 per cent. of its volume of concentrated sulphuric acid, by means of which unsaturated hydrocarbons and bases are removed, as well as certain types of sulphur compounds. Much sulphur dioxide is also liberated. After the removal of the tar or sludge produced by the action of the sulphuric acid, and also of the excess of acid, the oil is allowed to cool, whereby large quantities of crude, dark coloured paraffin wax are deposited. This is technically known as paraffin scale, and is purified by means of the sweating process (see p. 186).

In some processes the residuum is not submitted to distillation in vacuo, but is heated in iron stills, while superheated steam is introduced. The oil which distils over is thoroughly cooled or "chilled," whereby large quantities of very crude solid paraffin hydrocarbons are deposited. The non-solidified

oil is separated by means of a filter press, purified by successive treatment with sulphuric acid, water and caustic soda solution, and used as lubricating oil. In some cases it is redistilled.

The heating of the residuum is continued until the bottom of the retort is red-hot. By this means much of the non-volatile pitch which remains in the still is carbonized and converted into coke, which forms about 12 per cent. of the original crude oil. When this stage is reached dense yellow vapours issue from the retort, while a viscid resinous yellow substance condenses. This is known as "yellow wax," and contains anthracene in addition to several other complicated hydrocarbons. It is occasionally added to paraffin oil (kerosene) to increase its density.

CHEMICAL COMPOSITION AND PROPERTIES OF PARAFFIN WAX AND LUBRICATING OILS.

Paraffin wax consists of the higher members of the series C_nH_{2n+2} , and by means of fractional crystallization from suitable solvents, fractional fusion, etc., many of these have been isolated from it in a pure condition. Such are—

Tetracosane $C_{24}H_{50}$
 Hentriacontane $C_{31}H_{64}$
 Dotriacontane $C_{32}H_{66}$
 Tetratriacontane $C_{34}H_{70}$
 Pentatriacontane $C_{35}H_{72}$.

The melting-points of these hydrocarbons range from 50° to 76° . Pentatriacontane boils at 380° – 384° at 50 mm.

At a temperature considerably below its melting-point paraffin wax becomes plastic. It is insoluble in water, sparingly soluble in hot absolute alcohol, but readily so in ether, benzene and in mineral and essential oils.

When boiled with concentrated nitric acid it is oxidized, giving rise to succinic acid $COOH \cdot CH_2 \cdot CH_2 \cdot COOH$ and cerotic acid $C_{26}H_{53} \cdot COOH$. The production of the last-named substance indicates the presence in paraffin wax of the saturated hydrocarbon $C_{27}H_{56}$.

Potassium permanganate and also hot concentrated sulphuric acid attack paraffin wax slowly. In the melted condition it slowly interacts with chlorine. When heated with sulphur, sulphuretted hydrogen is evolved, and carbon deposited.

Vaseline.—The chief source of this complex mixture is the residue remaining in the still after *some* of the “still residuum” (B.P. above 300°C . at atmospheric pressure) has been removed by distillation in vacuo.

The residue is melted and passed through filters kept at about 50°C ., and containing well-dried bone black in fine granules. The filtrate is at first colourless, but becomes darker as more comes through. The portions lighter in colour are used as vaseline, while the less pure filtrate is employed exclusively as a lubricant under the name of *filtered cylinder oil*.

The process just described deals with the manufacture of vaseline from Pennsylvanian oil; a considerable amount is obtained, however, from Galician oils, which have been heated up to about 340°C .

The residues so obtained are dissolved in low-boiling petroleum, and decolorized by repeated treatment with animal charcoal. After filtering the solvent is distilled off, and the residue consists of vaseline.

Some Galician “residua,” after being filtered through bone charcoal, are distilled at 10–15 mm. pressure and the portion collected in the neighbourhood of 250° is used as vaseline.

Chemical Composition of Vaseline.—The composition of vaseline, much less the constitution of most of its constituent compounds, has not been satisfactorily determined.

It has been stated to consist of hydrocarbons (both normal and iso-) of the paraffin series, probably $\text{C}_{16}\text{H}_{34}$ to $\text{C}_{20}\text{H}_{42}$ together with certain unsaturated hydrocarbons.

Some consider it to be a mixture of various solid paraffins of low melting-point, others that it contains solid paraffins along with certain of the more volatile constituents of the oil from which it was obtained.

The discrepancies perhaps arise from the very different oil residues which are from time to time employed for its preparation and the differing temperatures to which these residues are subjected, as well as from the fact that some so-called vaselines are principally artificial mixtures of paraffin wax, ceresine (see page 74) and various oils.

Further Uses of Petroleum Products.—Many of the uses of petroleum products have already been indicated in the preceding pages; we may conveniently refer to others here.

The principle of the so-called Petrolite lamp is worthy of notice. A stream of air is drawn through a porous block heavily impregnated with that fraction of refined petroleum known as benzine.

The inflammable mixture of air and vapour thus obtained is burned under a Welsbach or other mantle as in an ordinary incandescent burner.

The lamp is stated to be quite safe since the inflammable vapour is produced by the draught created in the lamp chimney. If the lamp be overturned, the draught ceases and the flame is extinguished.

Those fractions of purified petroleum possessing rather a high boiling-point and viscosity are, after further very careful purification, used in the manufacture of hair tonics and the so-called "petroleum emulsions," and recently they have been used very largely as a successful substitute for drugs such as cascara sagrada, magnesium sulphate, etc.

The solid paraffins are used in the manufacture of candles and night-lights, while various other fractions of liquid petroleum find employment in the soap, varnish and metal-polish industries.

The volatile fractions are largely used as solvents in the process of waterproofing by means of rubber solution.

THEORIES AS TO THE ORIGIN OF PETROLEUM.

Only a very condensed account of the theories which have from time to time been proposed as to the mode of origin of petroleum will be given here. The experimental matter on which these theories have been founded must be even more briefly discussed. A comprehensive review of the whole question will be found in Sir Boverton Redwood's "Treatise on Petroleum," vol. i. p. 268.

There are three principal theories as to the origin of petroleum which have been very widely discussed. These may conveniently be designated as the Marine Animal, Terrestrial Vegetation, and Inorganic Theories.

According to the first of these, petroleum has been formed by the action of heat and pressure on the accumulated remains of marine organisms.

The second theory suggests that the remains of terrestrial vegetation such as coal or lignite may have given rise, under the influence of heat, pressure, or both, to the formation of petroleum.

The inorganic theories, for there have been several, have never been accepted by petroleum experts or by geologists, and some of them appear to be somewhat far-fetched.

It is a well-known fact that the action of water on metallic carbides produces hydrocarbons, *e.g.* aluminium carbide

gives methane; calcium carbide acetylene; manganese carbide methane and hydrogen; the carbides of lanthanum and thorium are stated to give rise to a mixture of ethylene, acetylene, methane and hydrogen on treatment with water, while uranium carbide gives in addition to volatile products certain liquid and solid hydrocarbons.

Mendeléef has suggested that petroleum has been formed by the action of water on iron carbide contained in the centre of the earth. The high temperature and pressure would, he considered, favour the condensation of the simpler hydrocarbons first formed to more complex products such as occur in petroleum. Iron carbide, it is well known, occurs in meteorites, so that its presence at the centre of the earth is by no means excluded.

Sabatier and Senderens in 1902 obtained a mixture of liquid hydrocarbons resembling Pennsylvanian petroleum by the action of nickel on a mixture of hydrogen and acetylene.

The reason why these theories have not been favourably regarded is not so much because they can be disproved, as on account of the large amount of evidence pointing to living matter as the material from which petroleum has been formed.

As regards the possibility of the formation of petroleum from coal it may be mentioned that the largest oil deposits are found in strata deposited in periods other than the coal age; these deposits are usually at considerable distances from coal measures. It is possible that a certain amount of petroleum may have arisen from terrestrial vegetation, but the quantity is probably small.

Many geologists have favoured the view that petroleum has been produced by the simultaneous action of heat and pressure on the accumulated remains of marine organisms, although opinions differ considerably as to the temperature and pressure at which the reaction is supposed to have taken place.

There is much evidence in support of this latter view, some of which may here be summarized. Petroleum is found in strata containing many animal remains but little or no plant residues. Again, by the distillation under pressure of a certain fish oil, Engler obtained a liquid resembling crude petroleum and from which he was able to isolate pentane, hexane, heptane, octane and nonane. The chemical reactions also indicated the presence of olefines, naphthenes and aromatic hydrocarbons.

Since nitrogenous substances are practically absent from

petroleum, Engler considers that the decomposition of the animal remains must have taken place in two or more stages. In the first of these preferential decomposition of the nitrogenous matter took place, owing possibly to bacterial action. Engler has obtained proof that such preferential decomposition of animal remains is not unknown in nature. (It is important to note that fossil bacteria have been found in oil-bearing strata.) From the residual fatty matter petroleum may then have been obtained as indicated above.

In conclusion, it should be pointed out that the organic theory of the formation of petroleum has recently received much support by the discovery of optically active products in crude petroleum, thus proving that living matter must at some time have participated in its formation (see page 22).

GLOSSARY OF TRADE NAMES FOR PETROLEUM PRODUCTS.

Albertite.—A product resembling and closely allied to Asphalt.

Asphalt.—A black viscous substance often to be met with at the outcrop of petroliferous strata. Has probably been formed as a result of the evaporation and atmospheric oxidation of exuding crude petroleum.

A very similar product may be obtained by blowing air through the hot residues left in petroleum stills.

Asphalt-rock.—The name applied to a stratum of sandstone or limestone when more or less saturated with asphalt.

Astatki.—*See* Ostatki.

Benzine.—That fraction of B.P. 70° – 120° obtained in the refining of petroleum. Heptane C_7H_{16} is the principal constituent of the benzine from Pennsylvanian oil. Totally distinct from the aromatic hydrocarbon benzene C_6H_6 .

Benzine, heavy.—*See* Ligroin.

Benzoline.—The more volatile portion obtained on redistilling benzine; B.P. about 70° – 95° . Often used as synonymous with benzine.

Ceresine.—Ozokerite freed from earthy matter and purified by means of warm fuming sulphuric acid.

Cymogene.—The liquid obtained by submitting the gases originally dissolved in crude petroleum to cold and pressure. B.P. 1° . Nearly pure butane. Used in certain types of refrigerators.

Earth wax.—*See* Ozokerite.

Gas, natural.—The gaseous products arising from petroleum wells. Rich in methane and ethane.

Gasoline.—That fraction of B.P. 40° – 70° obtained in the refining of Pennsylvanian oil. Consists largely of pentane C_5H_{12} , and hexane C_6H_{14} .

Gilsonite.—A product resembling and closely allied to Asphalt.

Jelly, mineral.—*See* Vaseline.

Kerosene.—That fraction of B.P. 150° – 300° obtained on distillation of American petroleum. Kerosene contains nonane C_9H_{20} , decane $C_{10}H_{22}$, etc., and is used as an illuminating oil.

- Ligroin.**—A term rather loosely applied. Usually denotes a refined petroleum distillate of B.P. 120° – 135° , but is occasionally applied to lower boiling fractions such as benzoline.
- Mineral burning oils,** suitable for burning with a wick, *e.g.* belmontine oil, cazeline oil, colzarine oil, mineral colza oil, mineral seal oil, mineral sperm oil, pyronaphtha (see also Kerosene).
- Motor spirit.**—The saturated aliphatic hydrocarbons of American oil, the polymethylenes from Baku oil or the unsaturated hydrocarbons derived from Shale oil, as well as benzene C_6H_6 and alcohol $C_2H_5.OH$, are employed in *internal* combustion engines. The boiling-points are usually *below* 120° .
- Naphtha.**—The less volatile portion obtained on redistilling benzine. Boils from about 95° to 120° . The term is unfortunately very loosely applied, and is synonymous with mineral naphtha. "Solvent naphtha" however is not a petroleum product (see page 230).
Green naphtha is one of the fractions obtained in the fractionation of crude shale oil.
- Ostatki.**—The residuum obtained in distillation of Russian petroleum. Much used as a fuel.
- Ozokerite.**—A peculiar wax-like substance which is forced up through the fissures of various strata. Is usually considered to have been formed by the gradual evaporation and oxidation of exuding petroleum. When purified by melting out from earthy matter and treating with fuming sulphuric acid is known as Ceresine.
- Paraffin oil.**—*See* Kerosene.
- Paraffin scale.**—Crude paraffin wax.
- Paraffin wax.**—The higher members of the series C_nH_{2n+2} which occur in American petroleum and in shale oil, *e.g.* $C_{24}H_{50}$. Used in the manufacture of candles.
- Paraffinum liquidum.**—The medicinal petroleum of the British Pharmacopœia. Sp. gr. 0.885–0.89. B.P. above 360° .
- Perfumery oil.**—Refined Russian petroleum. Sp. gr. 0.880–0.885. Used in pharmacy.
- Petrol.**—*See* Light petroleum; Benzine.
- Petrolatum.**—The Vaseline of the United States Pharmacopœia.
- Petrolatum liquidum.**—The medicinal high-boiling petroleum of the United States Pharmacopœia.
- Petroleum.**—In this book the term always indicates the crude untreated oil.
- Petroleum ether.**—*See* Gasoline or Benzine.
- Petroleum jelly.**—*See* Vaseline.
- Petroleum naphtha.**—Loosely employed; often denotes the first fraction (B.P. up to 150°) obtained on distillation of crude oil. Often applied to any low-boiling petroleum product.
- Petroleum spirit and Light petroleum.**—*See* Benzine, Benzoline, and Naphtha, with all of which the terms are more or less synonymous.
- Pitch.**—This term is loosely employed and may denote
(i) the residue remaining in the retorts after the distillation of crude coal tar;
(ii) a residue somewhat similar in appearance remaining after the distillation of crude petroleum;
(iii) the asphalt of the Asphalt or Pitch Lake in Trinidad.
- Polishing oil.**—That fraction of B.P. 130° – 160° obtained in refining of crude petroleum.
- Reduced oils.**—High-boiling petroleum oils which have been distilled in

vacuo and deprived of their dissolved paraffin wax by cooling and filtering through filter presses.

Residuum.—The residue obtained on the distillation of crude petroleum after the constituents boiling below 300° have been removed. Is worked up for paraffin wax, vaseline, and lubricating oils.

Rhigoline.—The most volatile liquid fraction obtained in the refining of crude petroleum. B.P. 18° , used as a local anæsthetic. Consists largely of pentane C_5H_{12} .

Shale ; Oil Shale.—A highly bituminous laminated substance containing about 80 per cent. of mineral matter, occurring in many parts of the world, but especially in the coal measures of the Lothians in Scotland.

Shale naphtha.—*See* Shale spirit.

Shale oil.—The somewhat tarry oil obtained when various bituminous shales are submitted to dry distillation. Contains unsaturated hydrocarbons and higher members of the series C_nH_{2n+2} .

Shale spirit.—The lower boiling fractions obtained in the refining of crude shale oil. Sp. gr. 0.70–0.76. Used as a motor spirit. Contains about 50–60 per cent. of unsaturated hydrocarbons.

Sherwood oil.—*See* Light petroleum and Petroleum ether.

Solar oil.—High-boiling fraction of Russian Petroleum used for fuel.

Solene.—*See* Gasoline or Petroleum ether, with which the term is synonymous.

Vaseline.—A mixture of high-boiling solid hydrocarbons of low melting-point, many of which belong to the series C_nH_{2n+2} . Sometimes contains unsaturated hydrocarbons.

Articles of the vaseline class are met with under the names **Ozokerine**, **Fossiline**, **Chrysine**, **Cosmoline**, **Saxoline**, **Geoline**, **Petrolina**, **Vaseline tallow**.

Yellow wax.—A viscous, semi-solid, difficultly volatile substance obtained on distillation of still residuum. Contains anthracene $C_{14}H_{10}$ and other hydrocarbons of complex structure.

CHAPTER III

PRECAUTIONS TO BE OBSERVED IN PRACTICAL WORK

It will be obvious that in dealing with inflammable liquids special care should be taken in guarding against the possibility of fire.

Special precautions must be observed during the manipulation of any of the following substances:—ether, carbon bisulphide, light petroleum, benzene, toluene, xylene, and any petroleum product boiling below 200° C.

None of these substances should ever be placed near a flame, except in the course of a distillation, nor should they even be allowed to remain upon the working bench.

During the distillation of all organic substances, the retort-stand carrying the distillation flask should be placed in a large tray. In case of an accident, the spreading of the hot liquid is thereby prevented.

When readily volatile, inflammable liquids are being distilled, it is absolutely necessary that the apparatus described on page 206, and indicated in the sketch, should be used. Special attention is directed to the rubber tube attached to the receiver. This should carry below the level of the bench, not, however, into the sink, any vapour which may have escaped condensation. It is, of course, extremely important that this outlet tube should be entirely free from obstruction.

It should be unnecessary to add that no receiver which is not fitted with a side-tube should *ever* be attached to the condenser by means of a singly-bored cork.

It will be obvious that in most operations in organic chemistry dry apparatus is required. Flasks, etc., are most conveniently dried by rotating slowly in a Bunsen flame and introducing a stream of air.

A very frequent source of fires is the reprehensible practice of adding porous tile to a hot liquid; sudden and violent

evolution of inflammable vapour frequently results, and a large volume of liquid is projected out of the flask.

During a distillation the flame should not be allowed to play upon the junction of the liquid and the wall of the glass vessel, since in such circumstances the flask almost invariably cracks. It is absolutely essential that a good supply of sand should be provided, and also blankets, in several well-known and accessible parts of the laboratory.

In case of fire, the burning apparatus or liquid should be completely covered with sand, by which means the air necessary to combustion is excluded. The use of water to extinguish burning liquids is usually undesirable, since the fire is thereby frequently distributed to places which would otherwise have escaped. Should the fire extend to the clothing of the operator, he should immediately wrap himself in a blanket. If help be available, he should be placed upon the floor and rolled in a blanket.

When a substance is to be heated in a stream of hydrogen it is extremely important that the apparatus should be completely freed from air before the heating is commenced. This can and must be ascertained in the usual way.

During vacuum distillation, great care must be taken that the apparatus is free from obstruction (as indeed in all distillations), and that a clear passage is open to the pump. The eyes should always be protected by a pair of goggles, preferably of gauze. Diminution of pressure should be carried out gradually, especially is this the case when the liquid in the apparatus is hot; otherwise sudden and violent boiling may occur.

In the determination of melting-points, a tray should always be placed under the vessel containing the sulphuric acid, and the heating carried out in such a manner that in case of an accident the operator will escape the action of the acid. The quantity of acid employed should be as small as is compatible with a slow rise of temperature.

It is extremely important that readily volatile substances such as petrol, benzene, etc., should not be poured down drains; neglect of this precaution may lead to a serious accident through the accumulation of inflammable vapour in the sewers.

CHAPTER IV

PREPARATION OF ALIPHATIC HYDROCARBONS

PREPARATION OF METHANE FROM SODIUM ACETATE

FOR the preparation of this gas, the sodium acetate employed must be perfectly free from water. This is accomplished by heating about 35 grams of the crystallized salt, which contains three molecules of water of crystallization, in an iron tray. The sodium acetate melts, and, after a few minutes, during which it should be well stirred, solidifies again. This indicates that the greater part of the water of crystallization has been expelled. The last traces are removed by re-melting completely, care being taken that the salt is not overheated, since under these conditions charring and evolution of inflammable gas takes place.

Twenty grams of the cold anhydrous salt are now taken and intimately mixed in a dry mortar with forty grams of soda lime, which should not be damp. The mixture is then strongly, but at first slowly, heated in a boiling-tube or round-bottomed flask which is fitted with a cork and delivery tube leading to a pneumatic trough containing water.

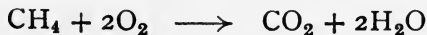


The boiling-tube or flask must be inclined so as to prevent any moisture which may condense from running back on to the hot surface of the vessel and cracking it. A few small jars of the gas are collected over water, and tested in various ways.

Before the heating of the mixture is discontinued the delivery tube must be lifted out of the trough, otherwise water will be sucked into the apparatus. This precaution must be observed in all similar cases.

(i) Apply a light to one of the jars. The gas burns with a flame which is slightly luminous, due to the presence of traces of impurities in the gas and to the sodium of the glass.

Pure methane burns with a non-luminous flame, producing water and carbon dioxide.



(ii) Shake up the contents of another jar with bromine water. Note that the colour of the bromine water remains almost unchanged.

(iii) Similarly agitate the gas with a solution of potassium permanganate which is sufficiently dilute to appear transparent. The colour is not discharged.

PREPARATION OF METHANE FROM ALUMINIUM CARBIDE.

The decomposition of aluminium carbide (Al_4C_3) by water gives rise principally to marsh gas, but other hydrocarbons,

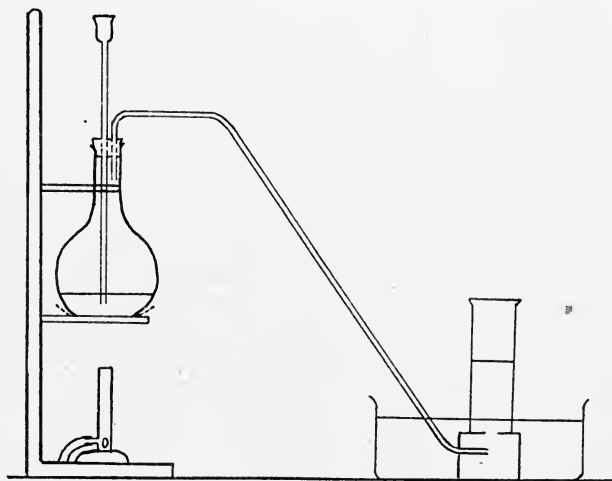
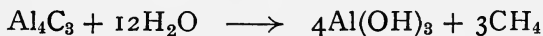


FIG. 1.—Apparatus for the preparation of methane from aluminium carbide.

such as acetylene, are produced in small quantities at the same time.



For the action of water on other metallic carbides, see page 73.

Place about 20 grams of aluminium carbide in a flask of about 200 c.c. capacity, fitted with a thistle funnel and delivery tube, as in the diagram, Fig. 1. Cover the carbide with water, and heat *very gently*, after shaking the mixture. Methane is evolved, and after allowing the gas to displace the air from the flask, is collected over water in the usual manner.

After collecting two jars of methane prepared in this

way, the gas is allowed to pass through two wash-bottles, the first of which contains bromine water and the other a strong solution of potassium permanganate.

By this means the unsaturated hydrocarbons will be removed.

Compare the luminosity of the flames of—

- (a) the purified gas,
- (b) the impure gas.

Shake jars containing (a) pure, (b) impure gas with a dilute aqueous solution of bromine. Compare the colours of the bromine solutions after the experiment.

Marsh gas or methane may also be obtained—

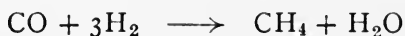
(i) by making an arc between carbon poles in an atmosphere of hydrogen—



(ii) By passing a mixture of sulphuretted hydrogen and carbon disulphide over heated metallic copper.



(3) By passing carbon monoxide or carbon dioxide mixed with hydrogen over finely-divided metallic nickel—



(See page 246.)

PREPARATION OF ETHANE, C_2H_6 .

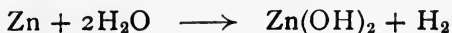
When ethyl iodide is reduced by means of nascent hydrogen the following reaction takes place:—



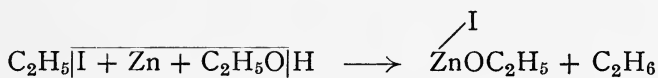
(This is an example of a general method for the preparation of a paraffin from an alkyl halogen compound.)

The reduction is effected by means of the “zinc-copper couple.”

Zinc, which has been treated with a solution of copper sulphate, is thereby covered with a thin film of metallic copper and decomposes water slowly, hydrogen being liberated—



or with a mixture of ethyl iodide and alcohol, the reaction is to be represented thus—



Place about 7 grams of zinc turnings in a small flask. Wash the zinc first with very dilute sulphuric acid (about 1 : 20), then three times with water. Cover the zinc with 60 c.c. of a three per cent. solution of copper sulphate, and allow the mixture to stand.

Copper is deposited on the zinc and the solution becomes colourless. When this is the case, pour off the liquid, treat the

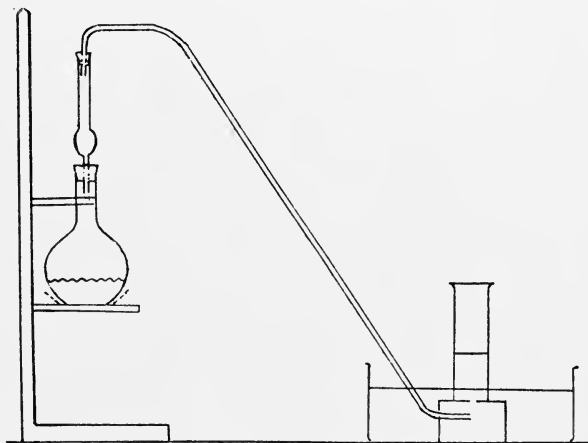


FIG. 2.—Apparatus for the preparation of ethane.

zinc-copper couple with another 60 c.c. of the copper sulphate solution, allow to stand till colourless, pour off the solution which now contains zinc sulphate, wash twice with water and finally once with methylated spirit.

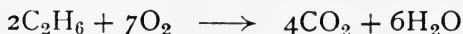
Dissolve 5 grams of ethyl iodide in about the same quantity of methylated spirit. Pour the mixture into the flask containing the zinc-copper couple. Fit the flask with a cork carrying a tall, so-called calcium chloride tube filled with more of the zinc-copper couple. (This serves to remove any ethyl iodide which may volatilize with the ethane.) Attach a delivery tube to the top of this tube, as in the diagram Fig. 2, and collect the evolved gas over water, after the air has been displaced from the flask.

By warming the flask gently the rate at which the gas is evolved is increased, but less gas will be obtained, and it will be less pure than if the reaction be allowed to proceed at the ordinary temperature.

Ethane is colourless, and has neither taste nor smell, it burns with a luminous flame, and does not combine directly with the halogens.

Shake up some of the gas with a small quantity of bromine water. The colour of the bromine is not removed. (Contrast ethylene, page 85.)

Apply a light to a jar of the gas, it burns with a *luminous* flame. Test for the presence of carbon dioxide after burning by means of lime water.



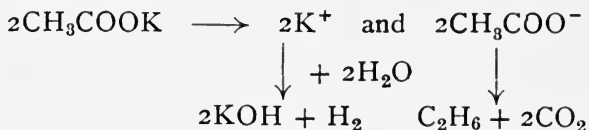
For the preparation of ethane by the reaction known as the Wurtz Synthesis, see Chapter I., page 4.

Ethane may also be prepared by the electrolysis of an aqueous potassium acetate solution.

At the cathode (–) we have the ions K^+ discharged, which on losing their charge react with the water and liberate hydrogen.

At the anode (+) the ions CH_3COO^- are discharged.

After neutralization of their electric charge they break up into CO_2 and the radicals $-\text{CH}_3$, which cannot, however, exist alone and unite, forming C_2H_6 ,



so that hydrogen is liberated at the cathode and ethane and carbon dioxide at the anode.

The electrolysis of the potassium salt of the monoethyl ester of malonic acid $\text{COOK} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ proceeds in a similar way.

In aqueous solution this substance gives rise to the ions—



The K^+ ion travels to the cathode, while the negative ion, on reaching the anode, loses CO_2 , giving rise to the radical $-\text{CH}_2 \cdot \text{COOC}_2\text{H}_5$, two of which unite to form

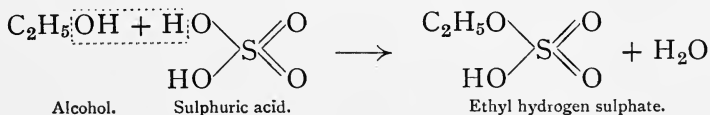
$\text{C}_2\text{H}_5\text{O} \cdot \text{OC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{OC}_2\text{H}_5$, a substance which is the diethyl ester of succinic acid.

Several other derivatives of dibasic organic acids can be obtained by similar electrolytic methods.

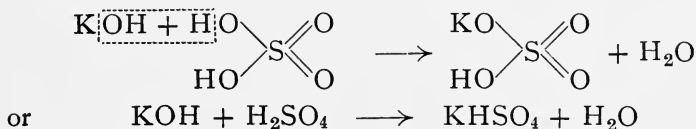
The electrolysis of the alkali salts of acids is in fact a very useful method in synthetic work, and finds a great many applications which cannot be described here.

PREPARATION OF ETHYLENE C_2H_4 .

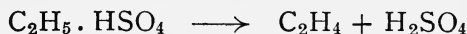
When ethyl alcohol and sulphuric acid interact, the first substance produced is ethyl hydrogen sulphate $\text{C}_2\text{H}_5 \cdot \text{HSO}_4$, thus—



Compare—



Ethyl hydrogen sulphate* is an unstable substance, and is decomposed by heating strongly into ethylene and sulphuric acid—

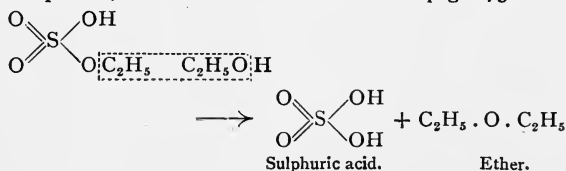


The preparation of ethylene by means of these reactions is carried out as follows—

An apparatus is set up as indicated in Fig. 3.

A mixture of 13 grams of alcohol (methylated spirit) and 75 grams of *commercial* concentrated sulphuric acid is placed

* The reaction between ethyl hydrogen sulphate and alcohol (the "continuous etherification" process) should here be referred to. See page 273.



in the round-bottomed flask, which should be of 1 – 1½ litres capacity.

Specific gravity concentrated H_2SO_4 = 1·84
 Specific gravity alcohol = 0·80

The tap funnel contains a mixture of 100 c.c. concentrated commercial H_2SO_4 and 50 c.c. methylated spirit. The flask and its contents are carefully and slowly heated on the sand-bath till a slight effervescence sets in, when the contents of the funnel are allowed to enter the flask drop by drop. After the effervescence has begun the heating must be regulated still

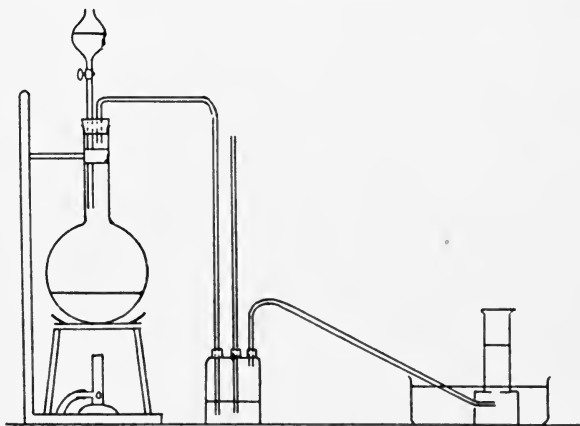
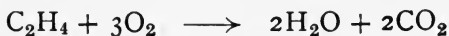


FIG. 3.—Apparatus for the preparation of ethylene.

more carefully, otherwise considerable frothing will occur and the flask may burst.

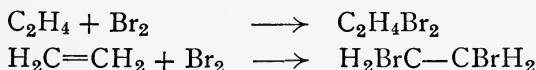
The gas, after bubbling through the solution of sodium hydroxide in the wash-bottle, to remove sulphur dioxide, is collected over water, at first in test-tubes, till on applying a light the gas burns quietly with a luminous smoky flame. If the flame be non-luminous ethylene is present only in small amount, and fresh test-portions must be collected.

Note the appearance of the flame of burning ethylene and compare it, if possible, directly with the flame of burning methane.

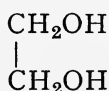


Shake up a jar of the gas with about 30 c.c. of bromine water, covering the jar with a glass plate.

Note. (i) the decolorization of the bromine water.
 (ii) the establishment of a partial vacuum.
 (iii) the production of oily drops of an almost colourless liquid, ethylene dibromide, or dibromoethane.



Shake up a jar of the gas with dilute potassium permanganate. The colour is discharged, a brown precipitate of hydrated manganese dioxide is produced, and, among other substances, glycol goes into solution.



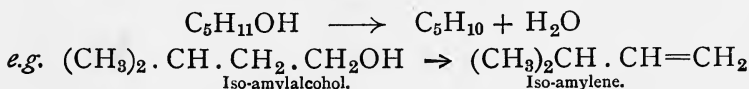
For an explanation of this reaction, see page 13.

Ethylene may also be prepared by heating alcohol with syrupy phosphoric acid H_3PO_4 , which extracts the elements of water $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$.

The homologues of ethylene may be prepared by an analogous method, namely, the elimination of water from the alcohols of the $\text{C}_n\text{H}_{2n+1}\text{OH}$ series.

Thus, amylene, or rather a mixture of isomeric amylenes, may be obtained by the action of anhydrous zinc chloride on crude amyl alcohol, which is a mixture of isomeric amyl alcohols.

The alcohol is allowed to stand for twenty-four hours with about one and a half times its weight of anhydrous zinc chloride. The mixture is then distilled from a sand-bath when that fraction coming over below 120° is collected separately and submitted to further fractionation.



PREPARATION OF ACETYLENE.

TO BE CARRIED OUT IN A FUME-CUPBOARD.

A few lumps of calcium carbide are placed in a dry flask of about 500 c.c. capacity. Most of the air is then displaced

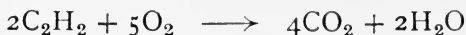
from the flask by means of a stream of coal gas introduced through a rubber tube reaching to the bottom of the flask. The cork carrying a dry dropping funnel and delivery tube leading to a pneumatic trough, is now inserted. The dropping funnel is fitted with a cork and tube, and more coal gas is passed in through this tube till the gas which bubbles through the water in the pneumatic trough is free from air.

Water is now allowed to drop slowly into the flask, when the following reaction takes place—



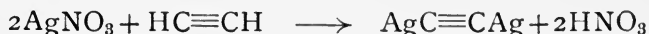
The complete displacement of air is necessary, since the carbide may contain calcium phosphide (derived from phosphates present in the lime and carbon used in its preparation), which with water yields a hydrogen phosphide, P_2H_4 , which inflames spontaneously in presence of air. The mixture of air and acetylene present in the flask at the commencement of the reaction might thus be caused to explode.

Collect the gas over water. Note the odour, which is partly due to the presence of impurities. Burn some of the gas. Note the luminosity of the flame and compare it with that of CH_4 , C_2H_4 , or C_2H_6 .

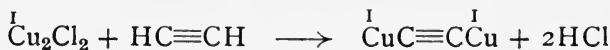


Shake up test-tubes full of the gas with—

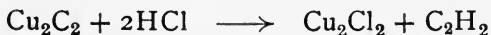
(i) AgNO_3 . A white precipitate of silver acetylide (or silver carbide), Ag_2C_2 , is produced.



(ii) Ammoniacal cuprous chloride solution. A *red-brown* precipitate of cuprous acetylide (cuprous carbide) is formed, Cu_2C_2 .



Filter off this precipitate and wash it well with water. Place the wet precipitate in a test-tube, add a few drops of concentrated HCl and gently warm. The precipitate dissolves and pure acetylene (odour less unpleasant) is evolved.



The metallic acetylides explode when dry. The formation

and subsequent decomposition of copper acetylide can be made use of to obtain pure acetylene from a gaseous mixture in which it occurs.

Allow a Bunsen burner to "strike back" for a few moments. Collect the fumes evolved in a glass jar. Add ammoniacal cuprous chloride solution and shake. The presence of acetylene is indicated by the formation of a red precipitate.

CHAPTER V

DISTILLATION

THEORETICAL

IT is a matter of everyday experience that if a liquid be left exposed to the air it evaporates, or passes into the state of vapour. It is equally apparent that different liquids evaporate at different rates under such conditions. If the temperature be raised, the rate of evaporation is increased, until, when a certain temperature is reached, which is different for practically every pure substance, the liquid is said to boil. At this temperature it passes freely into the state of vapour.

The tendency of liquids to pass into the vaporous condition is due to the fact that they possess what is known as a *vapour pressure*, which is due to molecules of the substance continually leaving the surface of the liquid, and in so doing exerting a pressure against that of the atmosphere. The readiness with which a substance is converted into the vaporous condition depends on the magnitude of its vapour pressure, compared with atmospheric pressure. The vapour pressure of a liquid increases with rise of temperature, until finally, when the liquid boils, its vapour pressure has become equal to that of the pressure of the atmosphere, and so at its boiling-point a liquid passes freely into the vaporous condition.

As soon as a pure liquid commences to boil in an open vessel its temperature remains constant; for although heat is being continuously supplied to the liquid, this heat, which is known as latent heat of evaporation, is required to effect the change in physical state of the substance. Thus to convert one gram of water at 100°C. into steam *at the same temperature* requires more than five times as much heat as is required to raise the temperature of the same weight of water from 0°C. to 100°C. (See page 293.)

Consider now the effect of pressure on the boiling-point of a liquid.

If the pressure on the surface of a liquid is greater than atmospheric pressure the liquid must be heated to a temperature higher than its boiling-point at atmospheric pressure, in order that the pressure of its vapour shall be sufficient to overcome the pressure on the surface of the liquid. That is, by increasing the pressure on a liquid its boiling-point is raised. Thus whilst the temperature of a liquid heated in a vessel open to the air never exceeds that of its boiling-point, in a closed vessel the liquid may be heated to a temperature very much above this, without the free disengagement of vapour, which constitutes boiling, taking place.

If, on the other hand, the pressure on the surface of a liquid be less than atmospheric pressure, the liquid will boil at a temperature below its boiling-point under ordinary conditions. This may be illustrated as follows:—

A small quantity of ether is placed in a filter flask containing a few small pieces of porous tile. The flask is closed by means of a rubber stopper and attached to a water pump. It will be noticed that on slightly reducing the pressure the ether begins to boil vigorously.

Both these principles of raising and lowering the boiling-points of liquids by variations in pressure are made use of in connexion with the distillation of petroleum, viz.: distillation under pressure and so-called vacuum distillation.

Vapour Pressure of Liquids at Temperatures below their Boiling-points.—Although the vapour pressure of a liquid at its boiling-point is equal to atmospheric pressure, it must be carefully noted that for *every* temperature all liquids have definite vapour pressures. This may be illustrated by reference to the following table which shows the pressures of *saturated** water vapour for every ten degrees from 0° to 100° C.—

Temperature.	Tension or pressure of aqueous vapour.	Temperature.	Tension or pressure of aqueous vapour.
0°	4·6	60°	148·8
10°	9·2	70°	233·1
20°	17·4	80°	354·3
30°	31·5	90°	525·5
40°	54·9	100°	760·0
50°	92·0		

These pressures are determined experimentally by finding to what extent the level of the mercury in a barometer is

* For the difference between a *saturated* and *unsaturated* vapour, see page 91.

depressed by the introduction of water and by surrounding the barometer tube with a wider tube, which contains a liquid or vapour at a known temperature. Thus, in the diagram, Fig. 4, the tube A represents an ordinary barometer.

In B water has been introduced, by means of a bent pipette, into a barometer similar to A. The water is present in excess on the surface of the mercury in the inner tube, so that the space above the mercury is saturated with water vapour. The outer jacket is filled with water at 50°C . In such a case the level of the mercury is depressed and the difference in height of the mercury column in the tubes A and B represents the pressure of saturated water vapour at 50°C . [It would be necessary to apply a small correction owing to the expansion of the mercury in the tube B.] In the tube marked C the arrangement is the same as in B except that the water in the outer tube at 50°C . is replaced by steam at 100°C . In this case the level of the mercury is depressed to the same height as that in the reservoir containing the three tubes. Since this is the case the pressure of the water vapour inside the tube must be the same as that of the atmosphere on the surface of the mercury in the reservoir.

It will be noticed that the term *saturated* vapour is used in connexion with the water vapour in the description of the above experiments. This vapour is in contact with the liquid (water) from which it is produced. It is of importance to distinguish between saturated and unsaturated vapours, and this difference may be illustrated as follows:—

If into the barometer tube B only a *very small* quantity of water had been introduced, the level of the mercury would not have been depressed to its full extent, and more and more depression would be produced on the addition of further quantities of water. At a certain point, however, the water ceases to evaporate, and the space above the mercury in the tube is then *saturated* with water vapour for that particular temperature 50°C . Before the point is reached at which the water ceases to evaporate, the space above the mercury contains *unsaturated* vapour, *i.e.* vapour which is not in equilibrium with the liquid from which it is produced.

It can be shown that unsaturated vapours possess physical properties which are very different from those of saturated vapours; thus the former obey the gas laws (effect of temperature and pressure on volume of vapour) while the latter do not.

It is, for example, impossible to compress a saturated vapour. If the tube represented by B, containing saturated

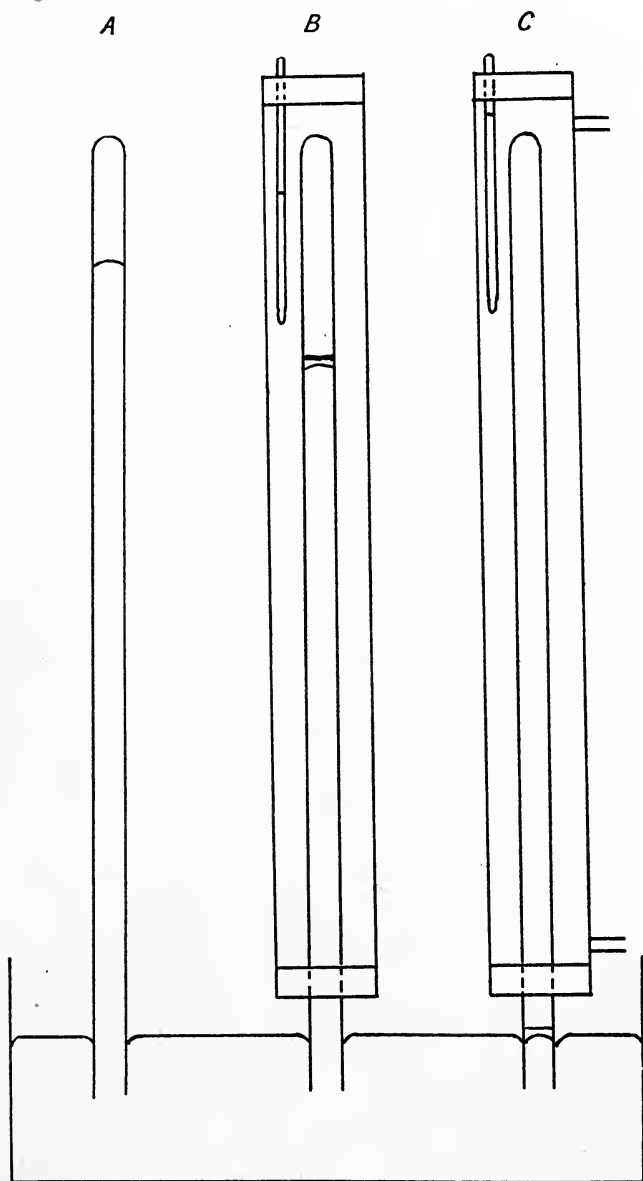


FIG. 4.—Apparatus for determining the vapour pressure of liquids at various temperatures.

vapour, were either raised or lowered in the reservoir, the difference between the height of the mercury inside and outside would remain the same, thus the volume of saturated vapour could be increased or diminished without any alteration in pressure. On the other hand, with unsaturated vapour, on raising the tube the difference in levels of the mercury would be greater than before, since on increasing the volume of an unsaturated vapour its pressure is diminished.

The Vapour Pressure of Mixed Liquids.—(a) *Non-miscible Liquids.*—If into the tube B, containing saturated water vapour, some liquid such as chlorobenzene, which does not mix with water, be introduced, the level of the mercury will be further depressed and the total observed pressure in the space above the mercury, will be equal to the sum of the pressures exerted by the water vapour and the chlorobenzene vapour separately; each liquid behaves, in fact, quite independently of the other, or as if each were evaporating in a vacuum. This case is exactly analogous with that of a mixture of gases, which have no chemical or physical action on each other. In such a mixture *each gas exerts the same pressure as if it alone occupied the entire vessel, and the total pressure is equal to the sum of the partial pressures of each gas.* This is known as Dalton's Law of Partial Pressures.

(b) *Partially Miscible Liquids.*—In the case of two partially miscible liquids, such as aniline and water, the vapour pressure will be found to be slightly less than the sum of the partial pressures of the two components but greater than that of either singly at the same temperature. This case is dealt with more fully under "Distillation with Steam," page 95.

(c) *Completely Miscible Liquids.*—In this case the vapour pressure of a mixture of two liquids is often found to lie between those of its constituents, but for certain mixtures it is sometimes greater and sometimes less than that of either constituent.

The relation between the vapour pressure of a homogeneous mixture of two liquids, at a constant temperature may be represented by means of curves, as shown in the diagram, Fig. 5, in which the ordinates represent vapour pressures and the abscissæ composition of the mixture.

The ordinate HC represents the vapour pressure of the substance B, and KD that of A.

The vapour pressures of mixtures of A and B at a given temperature are found to be represented by either

(1) A straight line CD.

(2) A curve CED, having a maximum at E.

(3) A curve CFD, having a minimum at F.

(1) As an example of the first case the mixture of methyl alcohol and water may be mentioned. In such a case the boiling-point of the mixture rises gradually. The vapour, and hence the distillate, will at first contain excess of the more volatile liquid, in this case methyl alcohol. A partial separation is thus effected, and if the first portion of the distillate be again distilled, a mixture still richer in alcohol will be obtained as the first portion of this new

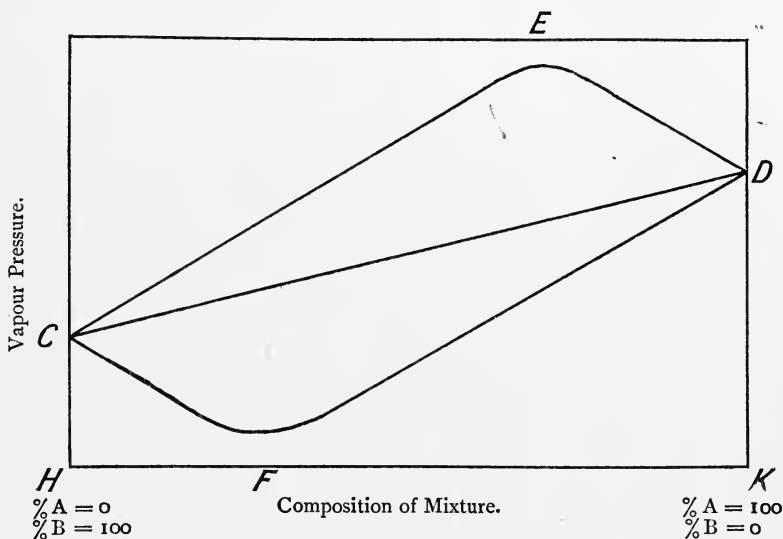


FIG. 5.—Vapour pressure curves of completely miscible liquids.

distillate. The separation of the constituents of a mixture by this means is termed *fractional distillation*. By applying this process to a mixture such as a petroleum oil, it is possible to isolate any particular hydrocarbon contained therein, if the distillation be repeated a sufficient number of times with suitable apparatus.

(2) If two liquids mixed together in a certain proportion can have a vapour pressure greater than that of either constituent, as represented in the diagram by the curve CED, then such a mixture of these constituents in this proportion must have a *minimum* boiling-point, which is lower than that of either constituent, since maximum vapour pressure corresponds to minimum boiling-point.

In such a case on distillation the mixture having the highest vapour pressure will pass over first, and the boiling-point will remain constant as long as this particular mixture of maximum vapour pressure is distilling over. A mixture of benzene B.P. 80° and methyl alcohol B.P. 65° , containing 60.5 per cent. by weight of the former has the greatest vapour pressure of any mixture of these two substances. On the distillation of any mixture of benzene and methyl alcohol the first portion of the distillate contains the substances in the proportion 60.5 per cent. by weight of benzene and 39.5 per cent. by weight of methyl alcohol, the mixture boiling at a constant temperature of 58°C .

(3) If the vapour pressure curve shows a minimum, as in CFD, a certain mixture of the two constituents must have a maximum boiling-point which is higher than that of either constituent.

On the distillation of such a mixture, the composition of the liquid remaining in the flask will alter in such a way that finally only the mixture of lowest vapour pressure, *i.e.* of highest boiling-point, will remain. This will then distil at a constant temperature, since the vapour above the liquid has the same composition as that of the liquid remaining in the flask.

A solution of hydrochloric acid containing 20.2 per cent. by weight of hydrogen chloride gas (B.P. -80°C .) has the lowest vapour pressure of any solution of this substance in water. A mixture of this composition boils at a constant temperature of 110°C . and the last portion of any solution of hydrochloric acid will boil at this temperature, since the composition of the solution will alter on distillation, until, finally that having the lowest vapour pressure will alone remain in the flask.

Effect of a Dissolved Solid on the Vapour Pressure of a Liquid.—It is found that the vapour pressure of a liquid is lowered by the solution of a solid in it, hence the boiling-point of the solution is higher than that of the pure solvent. It will be recalled that this is the principle underlying the method of determining molecular weights of substances in solution by the ebullioscopic method.

DISTILLATION WITH STEAM.

It frequently happens that although the vapour pressure of a substance at 100°C . is considerably less than atmospheric pressure, it may be completely vaporized by passing a

current of steam through the mixture in which it is contained. A practical application of this principle is met with in the removal of a substance such as aniline from a mixture of this substance with water (see page 205).

As previously explained, if two liquids do not mix when placed in contact with one another, the vapour pressure of each is quite unaffected by the presence of the other, and the boiling-point of such a mixture is that temperature at which the sum of the vapour pressures of the component liquids is equal to the pressure of the atmosphere.

Thus at a temperature of 91°C . the vapour pressure of chlorobenzene (B.P. 132°C .) is 216 mm. and that of water, with which it does not mix, at the same temperature is 546 mm. The sum of these two pressures $216 + 546 = 762$ is slightly greater than the ordinary atmospheric pressure; and it is found by actual experiment that a mixture of the two substances boils under ordinary conditions at a constant temperature between 90° and 91°C .

In the case of a mixture of aniline and water the substances dissolve each other slightly and the boiling-point does not remain quite as constant as in the previous case.

If we regard aniline and water as immiscible liquids the vapour pressure of such a mixture at 98° would be 42 mm. + 707 mm. = 749 mm. where 42 mm. represents the vapour pressure of aniline vapour at 98°C . and 707 mm. that of water vapour at the same temperature. So that under ordinary atmospheric pressure the mixture should boil at a temperature slightly above 98°C ., but owing to the slight miscibility of the constituents the boiling-point of the mixture is slightly higher than the calculated value.

By passing steam through this mixture of aniline and water the aniline vapour is continuously removed, more of the liquid aniline evaporates, and so finally it is entirely removed from the mixture.

The problem may also be regarded as follows:—

If the aniline could be placed in a flask from which the air has been entirely removed it would evaporate completely at, say 98°C ., if the flask were sufficiently large. The pressure inside the flask would be that of saturated aniline vapour at 98°C ., which equals 42 mm., provided the flask were only just large enough to convert all the aniline into saturated vapour. Regarding aniline and water as immiscible liquids, the vapour pressure exerted by the aniline in a mixture of the two substances will be the same in the presence of steam as if the aniline and its vapour were alone

present in the vessel. The *volume* of steam required to remove a given quantity of aniline will thus be equal to the volume of the vacuous flask, which would be required for the complete conversion of the aniline into saturated vapour at 98°C .

The relative *volumes* of steam and aniline vapour, which pass over on distillation, are directly proportional to the vapour pressures of the two substances at the temperature of the experiment; that is, the higher the vapour pressure of a particular constituent of such a mixture, the more of that substance is found in the distillate. Thus, in the mixture under consideration at 98°C . and 749 mm. pressure $\frac{42}{749}$ of the pressure is due to aniline vapour and $\frac{707}{749}$ due to water vapour. The volumes of aniline and water vapour which pass over on distillation are thus proportional to $\frac{42}{749}$ and $\frac{707}{749}$. In order to obtain the relative *weights* of these vapours it is necessary to multiply by the corresponding vapour densities, 46.5 and 9.

Hence the weights are proportional to $\frac{42}{749} \times 46.5$ and $\frac{707}{749} \times 9$, or 1 and 3.3, so that approximately one quarter by weight of the distillate under such conditions would be aniline.

The low vapour pressure of aniline is compensated for by the low value for the density of water vapour. Water is thus a particularly suitable substance for this "vapour" distillation. Other substances such as alcohol, toluene, etc., which might be used have molecular weights which are considerably greater than that of water and a much greater weight of one of these liquids would have to be vaporized in order to remove a given substance from a mixture, than is the case if steam be employed.

PRACTICAL.

Determination of the Boiling-point of a Liquid.

The liquid is placed in a clean and dry distilling flask containing a few small pieces of porous tile* and fitted with a cork carrying a thermometer, the bulb of which is just opposite the side tube of the flask as shown in the diagram, Fig. 6. A water condenser, Fig. 7, is attached to the side tube by means of a cork, in order to condense the vapour which will be produced on heating the liquid. It is extremely important that an ordinary flask should *not* be attached to the lower end of the condenser *by means of a singly bored*

* The object of adding this porous tile is explained on page 99.

cork, as if so there is no outlet for air and uncondensed vapour, and on heating some part of the apparatus will burst. If the liquid boils at a temperature above 120° C. a long glass tube (air condenser) may be substituted for the water condenser.

The flask is gently heated, using a water bath for liquids of low boiling-point and a small free flame for those boiling above 90° , and the liquid eventually boils. The heating is regulated so that from one to two drops of condensed liquid fall into the receiver per second. As soon as the temperature indicated by the thermometer is

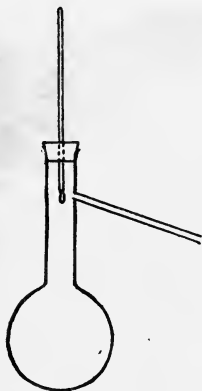


FIG. 6.—Distillation flask.

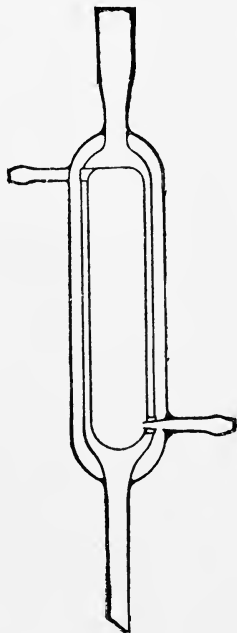


FIG. 7.—Davies condenser.

constant, this is registered as the boiling-point of the liquid.

The boiling-point of a *pure* liquid is always the same under the same pressure, and the constancy of the boiling-point of a liquid is made use of to ascertain its purity.

The boiling-points of alcohol (78°) and of aniline (183°) should be determined. See note *re* use of tray for distillation, page 77.

“Bumping,” its Cause and Prevention.—It frequently happens that if a liquid which is free from air be heated in a vessel of which the walls are very smooth, bubbles of vapour are formed only with difficulty, and the temperature of the

liquid may rise considerably above its boiling-point. At a certain point the liquid commences to boil vigorously and irregularly. Under such conditions the liquid is said to "bump."

If a globule of water be in suspension in an oil and the latter be heated, the temperature of the water globule may rise considerably above 100°C. , without the formation of bubbles of steam. Suddenly, however, on prolonged heating the water will be converted into vapour with explosive violence. This will be met with in connexion with the distillation of tar and of oils containing water.

For the prevention of bumping in the distillation of a homogeneous liquid, one of two methods is generally employed. Some fragments of broken porous tile, platinum foil or other material having rough edges are added to the liquid BEFORE HEATING. Bubbles of vapour form more easily on the rough surfaces, and the bumping is often prevented.

The other method consists in passing a slow current of air through the liquid during distillation. This is made use of in connexion with vacuum distillation, page 106.

Constant stirring will sometimes prevent "bumping." Thus, in one method for the determination of water in paraffin wax, the melted wax is kept at a temperature slightly above 100°C. and the mixture vigorously stirred to prevent spurting owing to sudden evolution of steam.

EXERCISES ON FRACTIONAL DISTILLATION.

Separation of a mixture containing light petroleum, toluene, nitrobenzene and vaseline.—Place 100 c.c. of the mixture in a dry distillation flask connected with a Davies Condenser, which by means of an adapter and tightly fitting corks communicates with a filter flask as in Fig. 40, page 206. The side tube of this filter flask should be provided with a rubber tube by means of which any uncondensed vapours may be led away to a level lower than that of the bench.

Some pieces of porous tile are now added, and the distilling flask closed with a well-fitting cork carrying a thermometer. The distillation flask is heated on a water bath, which is placed on an iron tray which should prevent the spread of any fire which might possibly ensue.

On gently heating the water bath, distillation begins at about 50° or lower, the thermometer slowly but steadily

rising all the time. The distillation should be carried on at such a rate that about one drop of liquid per second falls into the filter flask. When 65° is registered the burner should be temporarily extinguished and the condenser tilted so as to allow the liquid which remains in it to flow into the receiver (filter flask). The liquid collected there is then removed to a dry bottle, *corked* and labelled.

Fraction 1. B.P. up to 65° .

After removing the first fraction, the heating on the water bath is continued, and between 65° and 75° a further quantity distils over which is removed as before.

This is

Fraction 2. B.P. 65° – 75° .

When the temperature registered by the thermometer reaches 75° it will be found necessary to remove the water bath, and cautiously heat the flask with a small free flame, after drying it with a duster.

Above 75° the distillation slackens considerably, and after 80° is reached, the thermometer may even begin to fall. Another fraction 75° – 95° is now collected.

Fraction 3. B.P. 75° – 95° .

Above 95° the thermometer rises again and distillation becomes more rapid and a large fraction comes over between 95° and about 130° . The thermometer tends to remain constant for some time at or about 110° , the B.P. of pure toluene.

Fraction 4. B.P. 95° – 130° .

Above 130° * very little comes over for some time, and unless the heating be somewhat increased, the thermometer may fall several degrees, indicating the absence from the mixture in the distillation flask of substances boiling at temperatures about 150° to 180° .

Fraction 5. B.P. 130° – 190° .

A very large fraction distils between 200° and 210° , and consists of almost pure nitrobenzene. This fraction is collected separately.

Above 210° it will be found quite difficult to get the thermometer to rise and the distillation at ordinary pressures of more than a very small quantity of the vaseline remaining in the flask will be found impossible.

* At this temperature the water condenser should be replaced by an air condenser.

The fractions which should have been collected are indicated as follows:—

- | | | |
|------------------------------------|-------------------------------------|-------------------------------------|
| (1) up to 65° . | (2) 65° – 75° . | (3) 75° – 95° . |
| (4) 95° – 130° . | (5) 130° – 190° . | (6) 190° – 210° . |
| (7) above 210° . | | |

These various fractions are then redistilled from a smaller flask according to the method indicated below:—

Place fraction 1 in flask and heat very gently over a small free flame. Distillation will begin at about 45° and the fraction coming over between 45° and 55° [Fraction Ia] should be collected separately. After removal of this, the distillation is continued up to 65° , whereupon the fraction 2 is introduced into the distillation flask, after the condenser has been allowed to drain. On again distilling it will now be found that liquid comes over at a lower temperature than 65° , perhaps 50° (this phenomenon is characteristic of all fractional distillation operations), in which case all that distils below 55° should be placed along with fraction Ia. That coming over above 55° and up to 65° should be kept separately and labelled fraction Ib. B.P. 55° – 65° .

The distillation is continued, and at 75° the fraction 3 of B.P. 75° – 95° is added. Again, the liquid which will now distil will be found to have an initial boiling-point of about 70° – 75° , and the distillation is continued up to about 95° . Fraction IIa 65° – 95° . In this manner the distillation of all the fractions is carried out. Finally, after repeated distillation, a very large fraction is obtained boiling almost constantly at 110° and another boiling constantly at 204° . The intermediate fractions are relatively small in quantity, and by repeated fractional distillation can be further diminished. The isolation of a pure paraffin hydrocarbon from the fractions boiling below 75° is much more difficult and probably almost impossible with the quantities present in 100 c.c. of the mixture.

As a further exercise on fractional distillation 100 c.c. of paraffin oil may be distilled and fractions collected as follows:—

- | | | |
|---------------------------------------|---------------------------------------|----------------------------------------|
| (i.) up to 130° . | (ii.) 130° – 160° . | (iii.) 160° – 190° . |
| (iv.) 190° – 210° . | (v.) 210° – 230° . | (vi.) 230° – 250° . |
| (vii.) above 250° . | | |

Constant Boiling-point Mixtures (minimum).—Distil separately, using a water bath, 100 c.c. of each of two mixtures of

benzene and methyl alcohol containing different amounts of the two constituents.

The mixtures should have a constant boiling-point of 58° at the commencement of the distillation (see page 95).

The relative amounts of methyl alcohol and benzene in the distillate which comes over at 58° may be roughly estimated as follows:—

20 grams of the distillate should be shaken with about an equal quantity of water in a separating funnel, Fig. 8. The water dissolves the methyl alcohol and the benzene rises to the surface on allowing the mixture to stand. The aqueous solution is run off and the process repeated twice.



FIG. 8.—Separating funnel.

The benzene is then shaken in the separating funnel with some anhydrous calcium chloride to remove water, any solution of calcium chloride which forms should be run off and more of the drying agent added. Finally, the benzene is allowed to stand over anhydrous calcium chloride for about an hour, after which it is poured off into a previously weighed dry flask and its weight determined.

The percentage by weight of benzene in the mixture is thus found. The mixture should contain by weight 60.5 per cent. of benzene and 39.5 per cent. of methyl alcohol.

Constant Boiling-point Mixtures (maximum).—Distil two solutions of hydrochloric acid and note the gradual rise of the boiling-point until finally a constant temperature of 110° C. is attained.

Determine the percentage by weight of hydrochloric acid in the distillate collected at 110° by diluting 25 c.c. of the solution to 250 c.c. with water, and titrating portions of this solution with seminormal sodium hydroxide.

The amount of hydrochloric acid in the original distillate, collected at 110° should be 20.2 per cent. by weight.

FRACTIONATING COLUMNS, DEPHLEGMATORS.

In the distillation of a mixture containing liquids of which the boiling-points lie widely apart, it is often possible to

effect a practically complete separation by a single distillation.

In the case of a mixture such as petroleum, however, only a partial separation can be obtained in the ordinary way, since the boiling-points of the constituent compounds lie close together, and portions of the less volatile substances are carried over with the more volatile constituents.

It is possible to effect a more complete separation by attaching to the flask what is known as a fractionating column, the principle of which is as follows:—

The vapour rising from the surface of the liquid is partially condensed on the cold sides of the fractionating column. The vapour which is subsequently produced comes into close contact with this condensed liquid before it reaches the exit tube. By this means the less volatile constituents will be condensed and the vapour which escapes will be

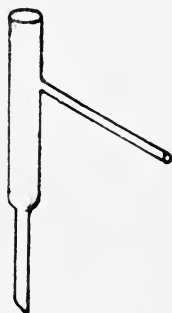


FIG. 9.—Still head.



FIG. 10.—Fractionating column (Young).



much richer in the more volatile constituent than that which left the liquid.

Various forms of fractionating columns are shown in the diagrams, Figs. 9 to 12.

The Hempel apparatus consists of an ordinary still head, Fig. 9, filled with glass beads or short pieces of glass tubing supported on a small gauze tray.

Fig. 10 represents one of Young's fractionating columns, shown also in section.

The Young and Thomas apparatus consists of platinum

or copper gauze trays, each carrying a short glass tube bent into a small hook. From ten to twenty of these trays are placed in a glass tube suitably constricted.

Fig. 11 represents the Glinsky Dephlegmator, which has glass beads at the constrictions in the tube and a reflux side tube. The Le Bel-Henninger Dephlegmator is shown in Fig. 12.

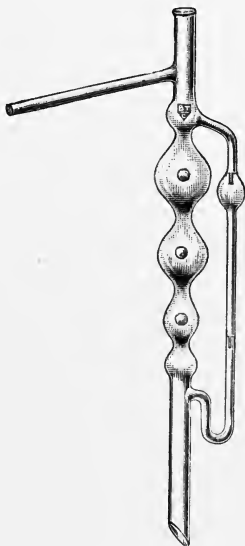


FIG. 11.—Glinsky dephlegmator.

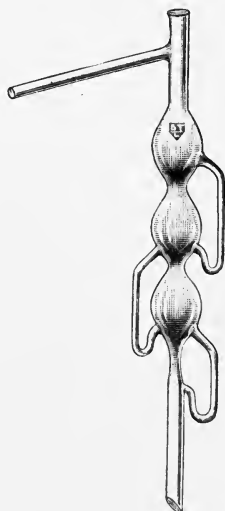


FIG. 12.—Le Bel-Henninger dephlegmator.

Fractionating columns in which the ascending vapour has to pass through shallow pools of the condensed liquid, and which have these reflux side tubes are in general known as dephlegmators.

These fractionating columns are fitted to an ordinary round-bottomed flask, without a side tube, and the condenser attached to the side tube of the column, the bulb of the thermometer being just opposite this side tube.

The different results obtained on the distillation of a petrol, with and without the use of a fractionating column, are illustrated in the annexed table taken from the results of Garry and Watson (*Four, Soc. Chem. Ind.*, 1904, p. 704).

	First drop condensed at	Volume per cent. of fractions.						
		Up to 70° C.	70-80.	80-90.	90-100.	100-110.	110-120.	120-140.
Plain distillation flask side tube 9.4 cm. up	63°C.	0.5	3.5	40.0	32.0	16.0	5.0	2.0
Le Bel-Henninger's dephlegmator (3 bulbs)	58°	2.0	17.0	26.0	30.0	15.0	4.0	4.0
Glinsky's dephlegmator (5 bulbs)	58°	1.0	12.0	35.0	28.0	15.0	4.0	4.0

The practical exercises described in the remainder of this chapter should be deferred until the student has had a considerable amount of experience in the manipulation of apparatus.

FURTHER EXERCISES ON FRACTIONAL DISTILLATION.

Distil 100 c.c. of the same sample of paraffin oil as previously used, from a flask fitted with a fractionating column, and compare the volumes of the fractions obtained over the same ranges of temperature.

Use the same fractionating apparatus for the distillation of various samples of petrol for a comparison of their volatility.

It should be noted that the dimensions of the distilling flask even in an ordinary distillation will also determine to a certain extent the composition of the distillate obtained over a particular range of temperature.

Thus, in the distillation of a crude oil, a standard Engler flask is often employed. This flask is represented in Fig. 13, and its dimensions are as follows:—

Diameter of bulb 6.5 cm. Neck of flask 1.6 cm. internal diameter and 15 cm. long. Side tube 9 cm. above the surface of the oil (100 c.c.), 10 cm. long and inclined at an angle of 75°.

During the distillation the flask is heated at first over a wire gauze, and subsequently by a free flame, the heating being so regulated that from 2 to 2.5 c.c. of the distillate pass over each minute. When 150° is registered (for first fraction) the burner is withdrawn

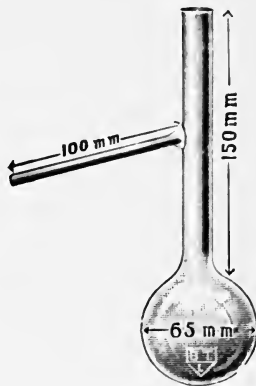


FIG. 13.—Engler distillation flask.

and the temperature allowed to fall at least 20° . The liquid is re-heated and again cooled, the process being repeated till no more distillate passes over at 150° . The distillation is continued and fractions collected for every 25° up to 300° , the process of cooling and re-heating being applied to each fraction as before.*

For details concerning the distillation of petroleum on a large scale, types of condensers employed, continuous distillation, etc., see Redwood's "Treatise on Petroleum."

VACUUM DISTILLATION.

This is carried out on the laboratory scale by means of an apparatus as shown in the diagram Fig. 14.

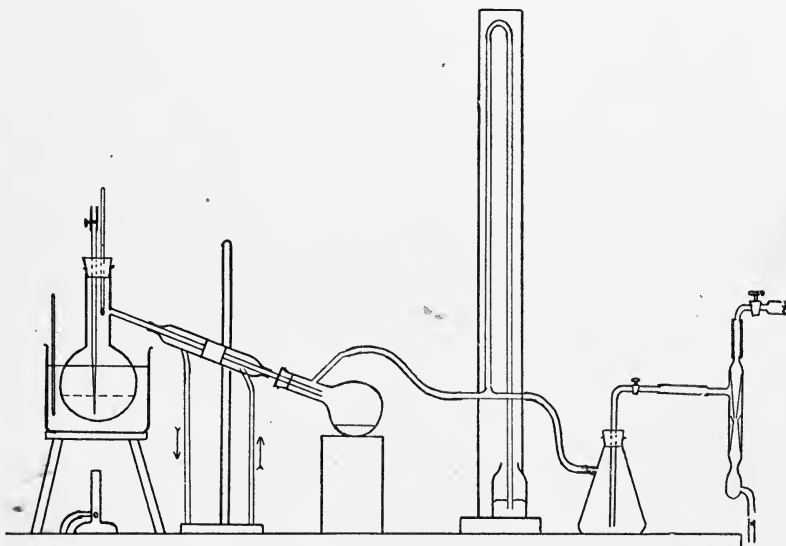


FIG. 14.—Apparatus for vacuum distillation.

A distillation flask of not more than about 250 c.c. capacity having a long side tube (larger flasks are liable to collapse at low pressures) is fitted with a two-holed rubber bung, a thermometer being fitted into one hole so that its bulb is just opposite the side tube of the flask. A piece of glass tubing drawn out to a

* The densities of the various fractions should be determined as described in Chapter VI. The gradual increase in density with rise in boiling-point is characteristic of a naturally occurring oil as distinct from many artificial mixtures.

fine point passes through the other hole and the capillary end of this tube reaches practically to the bottom of the flask when the bung is inserted. A small length of pressure tubing, carrying a screw clip, is attached to the upper end of this tube. The object of this glass tube is to allow a slow stream of air bubbles to pass through the liquid when the pressure is reduced and so prevent the bumping, which is very liable to occur in distillations under reduced pressure.

The long side tube of the distillation flask is fitted with the outer jacket of a water condenser, if the liquid to be distilled is not likely to condense by air cooling. Another distilling flask is attached to the end of the side tube by means of a rubber bung, and the side tube from this flask is attached to the water pump, through a suitable manometer; all the connexions being made by means of pressure tubing.

It is extremely important to notice that only round-bottomed flasks should be used in a vacuum distillation. Ordinary flat-bottomed or conical flasks will collapse if the pressure inside them is considerably reduced.

If it is required to separate the distillate into two or more fractions, use is made of what is known as a distillation "pig," the construction of which is shown in the diagram Fig. 15.

This "pig" is fitted to the end of the side tube of the distillation flask, and by turning it slightly after a certain fraction has been collected in one of the round-bottomed flasks or thick walled glass tubes attached, another portion of the distillate may be collected. Other forms of apparatus for effecting this object, together with a simplified form of manometer for distillation at low pressures, are shown



FIG. 15.—Receiver for fractional vacuum distillation.

in Cohen's "Practical Organic Chemistry" (1910), page 86.

Before commencing a vacuum distillation, make sure that all connexions are air-tight by turning on the water pump slowly, taking care that all taps connected with the apparatus are open, and noting the pressure indicated by the manometer. It is important that exhaustion, and admission of air after exhaustion, should be carried out slowly, otherwise part of the apparatus may burst.

It will be apparent that at any time the pressure in the apparatus cannot be less than the pressure of saturated water vapour at the temperature of the water, if a water pump is employed, and on this account it is occasionally necessary in

special cases to employ a mercury pump, by means of which the pressure is reduced still further.

In a vacuum distillation the flask containing the liquid to be distilled is heated either in an oil or fusible metal bath.

In the manometer shown in the diagram the pressure inside the apparatus is the difference between the height of the barometer and the height to which the mercury rises in the manometer tube.

By means of the apparatus described above, carry out a vacuum distillation of glycerol. Make a careful note of the relation between the temperature at which the liquid boils and the pressure indicated by the manometer.*

A fractional vacuum distillation of a substance such as vaseline or a heavy lubricating oil should also be performed.

For practical applications of vacuum distillation to the refining of petroleum, see Redwood's "Treatise on Petroleum," vol. ii. p. 15.

For further information on Distillation in general, see Thorpe's "Dictionary of Applied Chemistry," and Young's "Fractional Distillation" (Macmillan).

* The figures given on page 90 for the pressure of saturated aqueous vapour at different temperatures also denote the boiling-point of water under various reduced pressures.

CHAPTER VI

DETERMINATIONS OF DENSITY, VISCOSITY AND MELTING POINT. FRACTIONAL CRYSTALLIZATION

RELATIVE DENSITY, OR SPECIFIC GRAVITY

THE relative density or specific gravity of a substance is the weight of a certain volume of that substance compared with the weight of an equal volume of a standard substance. The generally accepted standard substance for solids and liquids is distilled water at a temperature of 4°C ., since at this temperature 1 c.c. of water has its greatest mass, 1 gram. The relative density of a solid or liquid at a given temperature is therefore the weight of a certain volume of the substance, at this temperature, divided by the weight of an equal volume of water at 4°C .

It is more usual to determine the relative density at the ordinary temperature, 60°F . ($= 15.5^{\circ}\text{C}$.), than at 4°C .

Relative Densities of Solid Substances heavier than, and insoluble in, Water.—To determine the relative density of a solid, it is necessary, first to weigh it in the ordinary way and then to weigh it immersed in water, by suspending it from the beam of a balance by means of a fine fibre, the water being contained in a beaker supported on a wooden bridge over the scale pan.

By Archimedes' principle, the loss of weight in water of the solid is equal to the weight of the water displaced, which is the weight of a volume of water equal to the volume of the solid.

Hence, if M = weight of solid in air

and M_1 = " " " water at 15.5°C .

$M - M_1$ = loss of weight in water
= weight of water displaced

\therefore The relative density of the solid at 15.5°C . $= \frac{M}{M - M_1}$

This gives the density of the body at 15.5°C. relative to that of water at 15.5° , denoted $d_{15.5^{\circ}}^{15.5^{\circ}}$. If the density of the body at 15.5°C. relative to that of water at 4°C. , were required, $d_{4^{\circ}}^{15.5^{\circ}}$, the above result would have to be multiplied by 0.9991, which is the density of water at 15.5°C. (water at $4^{\circ}\text{C.} = 1$).

Relative Density of Solid Substances lighter than, and insoluble in, Water.—The substance is weighed in air, and then attached to a solid (the sinker) sufficiently heavy to cause it to sink in water.

If M = weight of substance in air
and L = its loss of weight in water, *i.e.* weight of water displaced by it

$$\text{its relative density} = \frac{M}{L}$$

To find the value of L

Let S = weight of sinker in water

C = combined weight of sinker and substance in water

Then $C - S$ = weight of substance in water

The loss of weight of the substance in water (L)

= its weight in air (M) minus its weight in water ($C - S$).

$$\therefore L = M - (C - S)$$

$$\text{or } L = M - C + S$$

$$\therefore \text{Relative density of the substance} = \frac{M}{L} = \frac{M}{M - C + S}$$

For example—

The weight of a piece of wax in air = 20.24 grams

Weight of sinker in water (at 15.5°C.) = 46.36 grams

Weight of sinker and wax in water (at 15.5°C.) = 44.16 grams

\therefore Weight of wax in water = (44.16 - 46.36) grams

loss of weight of wax in water = 20.24 - (44.16 - 46.36) grams

$$= 20.24 + 2.2$$

$$= 22.44$$

$$\text{Relative density of wax (at } 15.5^{\circ}\text{C.)} = \frac{20.24}{22.44} = 0.902$$

(that is, taking the density of water at 15.5°C. as 1.)

Relative Densities of Liquids.—The most accurate method of determining the relative density of a liquid is by direct weighing of equal volumes of the liquid and of water. This

is generally accomplished by means of a so-called specific gravity bottle or pyknometer.

A form of specific gravity bottle suitable for the determination of the relative density of a volatile liquid is shown in Fig. 16.

This consists of a thin glass flask, or bottle, fitted with an accurately ground blown-glass stopper. The neck of the flask is constricted below the stopper, and a mark etched upon it enables the operator to fill the bottle with the same volume of liquid each time it is used.

Before use the bottle is cleaned, and dried in the steam oven. When taken from the steam oven, a stream of air should be drawn through the bottle by means of a glass tube which passes to the bottom; otherwise water vapour may condense on the inside. This is continued until the bottle is quite cold, when the stopper is inserted and the whole weighed accurately. It is then filled with distilled water at 15.5°C ., placed in a bath at the same temperature and kept there for about 15 to 20 minutes. Any excess of water is removed by means of a pipette until the meniscus is just level with the mark on the neck of the bottle. The dry stopper is then inserted, and the bottle carefully dried and weighed.

The difference between the weights of the bottle full and empty gives the weight of water at 15.5°C .

The bottle is now emptied, dried, and filled in the same way with the liquid under examination, the temperature of the liquid being adjusted to 15.5°C . as before.

The weight of a volume of liquid equal to the volume of the water is thus found, and hence its relative density may be determined.

In the determination of the density of a specimen of benzene in a 50 gram specific gravity bottle,

the weight of the bottle empty = 21.6227 grams

" " " " filled with
distilled water at 15.5°C . = 71.6237 "

weight of water = 50.0010 "

Weight of bottle filled with benzene at 15.5°C . = 65.9236 grams

" " " empty = 21.6227 "

Weight of benzene = 44.3009 "

Relative density of benzene $d_{15.5^{\circ}}^{15.5^{\circ}} = \frac{44.3009}{50.0010}$
= 0.886

Another form of specific gravity bottle suitable for non-volatile liquids is shown in Fig. 17.

The bottle is fitted with a perforated stopper and can be completely filled with the liquid or with water, the excess flowing through the hole in the stopper.

A convenient form of apparatus for the determination of densities at high temperatures is shown in Fig. 18.

The apparatus is known as a Sprengel tube or pyknometer.

The capillary tube, on which the mark is made, is expanded into a bulb which allows for expansion of the liquid when the temperature rises.

For a density determination with this apparatus the tube must first be filled with distilled water, and then with the liquid under examination.

The dried and weighed tube is filled with liquid by attaching one limb to a water pump. It is then supported in a beaker of water at the required temperature.



FIG. 16.—Specific gravity bottle.



FIG. 17.—Specific gravity bottle.



FIG. 18.—Pyknometer.

The volume of the liquid is adjusted to the mark when the temperature has become constant, by supporting the tube so that the capillary having the bulb is vertical, and removing liquid from the other capillary by means of filter paper.

When the apparatus is replaced in the normal vertical position, the liquid rises in the capillary having the bulb and so sinks from the end of the other. By this means it is protected from evaporation during weighing. As a further precaution glass caps are sometimes placed over the capillary ends.

Densities of Liquids by means of the Specific Gravity Balance.—The principle of these balances is as follows :—

A plummet is counterpoised when immersed in water, so

that, if it be immersed in a liquid lighter than water, weights must be removed from the beam of the balance on the side from which the plummet is suspended, in order to restore equilibrium. On the other hand, if it is suspended in a liquid which is heavier than water, extra weights must be added to restore equilibrium.

The Westphal Specific Gravity Balance is shown in Fig. 19.

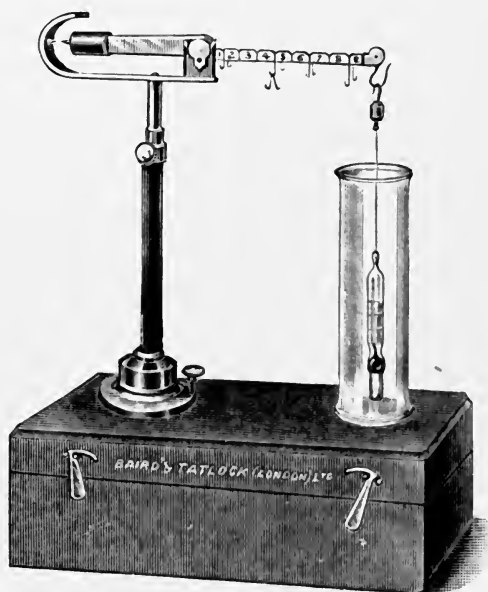


FIG. 19.—Westphal specific gravity balance.

The balance is adjusted so as to be in equilibrium when the plummet is suspended in the *air*. When the plummet is placed in *water* at 60° F. the largest rider has to be suspended from the same hook as the plummet in order to restore equilibrium; that is, the weight of the largest rider is equal to the weight of the water displaced by the plummet.

If the plummet is now suspended in another liquid at 60° F. and it is found that equilibrium is restored when the rider is suspended from the notch marked 8, since the beam is divided into ten equal parts, the weight of liquid displaced must now be $\frac{8}{10}$ or 0.8 of what it was in the former case. Equal volumes of the liquid and of water are displaced in each case, so that the weights of these equal volumes are 8 : 10 or the

specific gravity of the liquid at 60° compared with water at 60° is 0.8.

If it be found that equilibrium is established when the rider is between the divisions 7 and 8, it is placed on the notch 7, and the next largest rider, which is one-tenth the weight of the first, is placed on the beam.

It may be found that equilibrium is established when this rider is also placed between notches 7 and 8. In this case it is suspended from the other rider on notch 7. The third and fourth riders, which are respectively $\frac{1}{100}$ th and $\frac{1}{1000}$ th, the weight of the first, are then employed, and if equilibrium is established when the former is on notch 3 and the latter on notch 4, the relative density or specific gravity of the liquid is 0.7734.

In order to use this balance it is necessary that the viscosity of the liquid shall be such as not to interfere with the free movement of the plummet. It is possible with this instrument to obtain densities accurate to the third place of decimals.

Specific Gravity by means of Hydrometers.—The principle of the hydrometer is the same as that underlying the specific gravity balance. The denser a liquid the more does a floating body project from its surface.

Many kinds of hydrometers are in use, the simplest being those from which the specific gravity of the liquid is read off directly from the scale number which is level with the surface of the liquid when the hydrometer is floating freely.

Such hydrometers are made in a series. One instrument may read from sp. gr. 0.780 to 0.800, another from 0.800 to 0.820, and so on. The scale of such hydrometers being about six inches long, the specific gravity can be obtained accurately to the third place of decimals.

The instruments are usually made so that the reading is 1.0 for distilled water at 15.5° C. In the case of other hydrometers such as the Twaddell and Beaumé instruments, the scales are quite arbitrary.

Thus in the Twaddell hydrometer, Fig. 20, for liquids heavier than water, to convert to specific gravity, multiply the degrees Twaddell by 5, add 1000, and divide the result by 1000.

Example :—

$$30^\circ \text{ Twaddell} = \frac{150 + 1000}{1000} = 1.15 \text{ specific gravity at } 15.5^\circ \text{ C.}$$

To convert Beaumé degrees to specific gravity, for liquids

lighter than water, add 130 to the Beaumé reading and divide the sum into 140.

Example :—

$$20^{\circ} \text{ Beaumé} = \frac{140}{150} = 0.9333 \text{ specific gravity at } 15.5^{\circ} \text{ C.}$$

Unfortunately, in some makes of the Beaumé hydrometer the factor given here as 130 is as high as 135, and in the United States a different table is employed for converting degrees Beaumé to specific gravity. [See Hicks' "Mineral Oil Testing." C. Griffin & Co.]

The relative densities of different specimens of oil should be determined by the various methods, and the results compared.

If only a very small sample of oil is available, its relative density may be found by mixing alcohol and water in such proportions that, after cooling to the ordinary temperature, on placing a drop of the oil in the mixture it neither sinks nor rises. The relative density of the mixture is then determined by one of the foregoing methods.

If the sample has a relative density greater than unity, a salt solution may be employed in the same way.

VISCOSITY.

Viscosity is the property possessed by matter in virtue of which it resists the action of forces tending to produce in it a change of shape. It differs, however, from elasticity in that it does not imply any power of recovery when the distorting force is removed. This property is generally associated with liquids.

The magnitude of the viscosity of various liquids varies greatly, thus ether has little viscosity, whilst with substances such as treacle and pitch the viscosity or internal friction approximates to that of solids.

For the present purpose it is sufficient to compare the viscosities of liquids, and not to determine their absolute values.

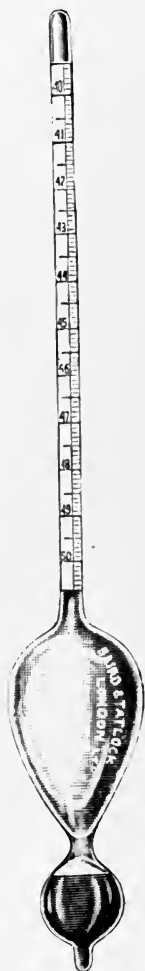


FIG. 20.—
Twaddell
hydrometer.

The so-called *coefficient of viscosity* of a liquid, denoted η , is defined as the force required to move a layer of unit area of the liquid, through a distance of unit length, past another layer of the liquid separated from it by unit distance.*

Its value can be calculated from the rate of outflow from a tube and

$$= \frac{\pi p r^4 t}{8 \nu l}$$

where p is the pressure under which the outflow takes place, r the radius of the tube, t the time of outflow, ν the volume of liquid discharged, and l the length of the tube.

If, then, equal volumes of two liquids, A and B, be allowed to flow through the *same* tube, the ratio of the coefficients of viscosity will be—

$$\frac{\eta_A}{\eta_B} = \frac{\frac{\pi p_A r^4 t_A}{8 \nu l}}{\frac{\pi p_B r^4 t_B}{8 \nu l}}$$

or, since r , ν , and l are the same in both cases

$$\frac{\eta_A}{\eta_B} = \frac{p_A t_A}{p_B t_B}$$

The pressures under which the outflow takes place are proportional to the densities of the liquids, or

$$\frac{\eta_A}{\eta_B} = \frac{t_A d_A}{t_B d_B}$$

where d_A and d_B are the densities of the two liquids. The viscosities of the two liquids can thus be compared by noting the time of outflow of equal volumes of each from the same apparatus and by determining their densities.

It should be noted that the viscosities of substances, especially of oils, are greatly diminished by increase of temperature (see page 323); it is therefore extremely important, in connexion with viscosity determination, to specify the temperature at which the experiment is carried out.

The determination of the viscosity of oils is primarily of importance in connexion with their use as lubricants; the

* For further information regarding the theory of viscosity, text-books of Physics should be consulted.

mobility of an oil has, however, to be taken into account with a view to its use as a fuel.

In practice the viscosity of an oil is compared with that of a standard substance, generally rape oil, by noting the times required for the flow of equal volumes of the two oils at known temperature through a given orifice in a specified

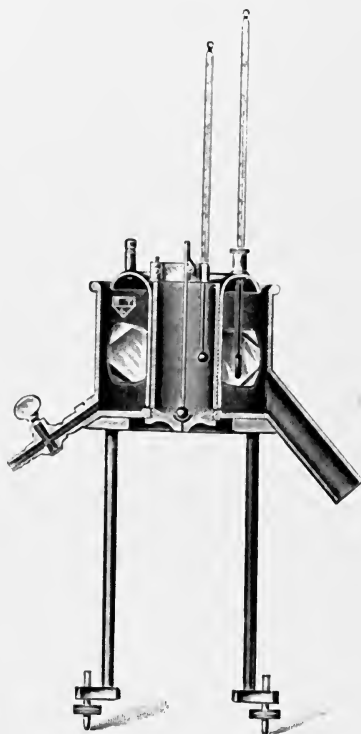
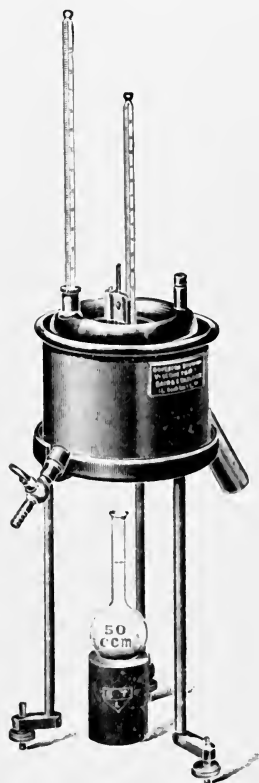


FIG. 21.—Redwood viscometer. FIG. 22.—Redwood viscometer (section).

apparatus. The form of apparatus usually employed for lubricating oils in this country is that known as the Redwood Viscometer, shown in Fig. 21, and in section in Fig. 22; and for fuel oils, that known as the Redwood Admiralty pattern Viscometer, Fig. 23.

The Redwood Viscometer.—(*Journal of the Society of Chemical Industry*, 1886, vol. v. p. 126.)

Description of the apparatus taken by permission from J. A. Hicks' "Mineral Oil Testing" (C. Griffin).

The instrument, Fig. 21, consists of a silvered brass oil-cylinder, furnished with an agate jet, and surrounded with a copper bath. A copper tube, closed at the lower end, projecting at an angle of 45° from the side of the bath, near the bottom, provides a means of heating the bath liquid, and by the use of a revolving agitator, which forms part of the apparatus, the heated liquid rising from the copper tube can be uniformly distributed through the bath. The agitator carries a thermometer to indicate the temperature of the bath. The oil-cylinder is furnished with a stopper, consisting of a small brass sphere attached to a wire, the sphere resting in a hemispherical cavity in the agate jet. A short standard, attached to the oil-cylinder, carries a clip to support a thermometer in the oil. Inside the oil-cylinder, and at a short distance from the top, is fixed a small bracket, terminating in an upturned point, which forms a gauge of the height of the oil level. The instrument is supported on a tripod stand provided with levelling screws.

The bath is filled with a suitable liquid to a height roughly corresponding with the point of the gauge in the oil-cylinder. Water answers well for the temperature up to 200° F., and for higher temperatures a heavy mineral oil may be used. The liquid having been brought to the required temperature, the oil to be tested, previously brought to the same temperature, is poured into the oil-cylinder, until the level of the liquid just reaches the point of the gauge. A narrow-necked graduated flask of 50 c.c. capacity is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop watch at the same time started, and the number of seconds occupied in the outflow of 50 cubic centimetres noted. It is of the greatest importance that the oil-cylinder should be filled exactly to the point of the gauge, after inserting the thermometer, and that the given temperature should be precisely maintained during the experiment, a difference of half a degree F. making an appreciable alteration in the viscosity of some oils. It is also essential that the oil should be quite free from dirt or other suspended matter, and from globules of water, as otherwise the jet may be partially obstructed. If the oil-cylinder requires to be wiped out, paper, rather than cloth, should be employed, as filaments of the latter may be left adhering. When oils are being tested at temperatures much above that of the

laboratory, a gas flame is applied to the copper heating tube, and the agitator kept in gentle motion throughout the experiment.

Note :—The jet should be carefully examined before the apparatus is used, and, if necessary, should be cleaned by passing a piece of tissue paper through it. The apparatus should be adjusted by means of the levelling screws, so that a spirit level placed on the top of the oil-cup shows it to be horizontal.

Method of Expressing the Results of Viscosity Measurements.—Redwood recommends that the number of seconds occupied in the outflow of 50 cubic centimetres of the oil under examination should be multiplied by 100 and divided by 535 (the number of seconds occupied in the outflow of 50 cubic centimetres of average refined rape oil at 60° F.*). The resulting figures should then be multiplied by the specific gravity of the oil under examination at the temperature of the experiment, and divided by 0.915 (the specific gravity of refined rape oil at 60° F.) the necessary correction for specific gravity being thus made, the final figures will express the viscosity of the oil, at the temperature of the test, in terms of the viscosity of refined rape oil at 60° F.

The Redwood Viscometer, Admiralty pattern, for testing Oil Fuel.—The following description of the apparatus is adapted, by permission, from that given in J. A. Hicks' "Mineral Oil Testing" (C. Griffin) and from details supplied by the makers.

The apparatus, Fig. 23, consists of a silvered brass oil-cylinder, fitted at its base with an agate jet of standard bore (5 cm. long and 3.5 mm. diameter). This agate jet is encased in a stout brass tube which is screwed at its end and fits into the centre of the outer vessel. This outer vessel is of spun copper, lined on the outside with oak, and fits on to a brass levelling stand. Two low-temperature thermometers graduated 0°–70° F. are employed. A ball valve is used for closing the agate jet, and the instrument is fitted with a revolving agitator.

The outer vessel or bath is packed with broken ice to a height roughly corresponding with that of the gauge-point in the oil-cup.

The oil to be tested must be free from water, dirt, and matter in suspension, and should be maintained at a temperature of 32° F. for at least six hours immediately before it is tested.

* This should be verified by experiment.

The thermometer is supported in the oil-cup by means of the clip, so that its bulb rests on the bottom of the

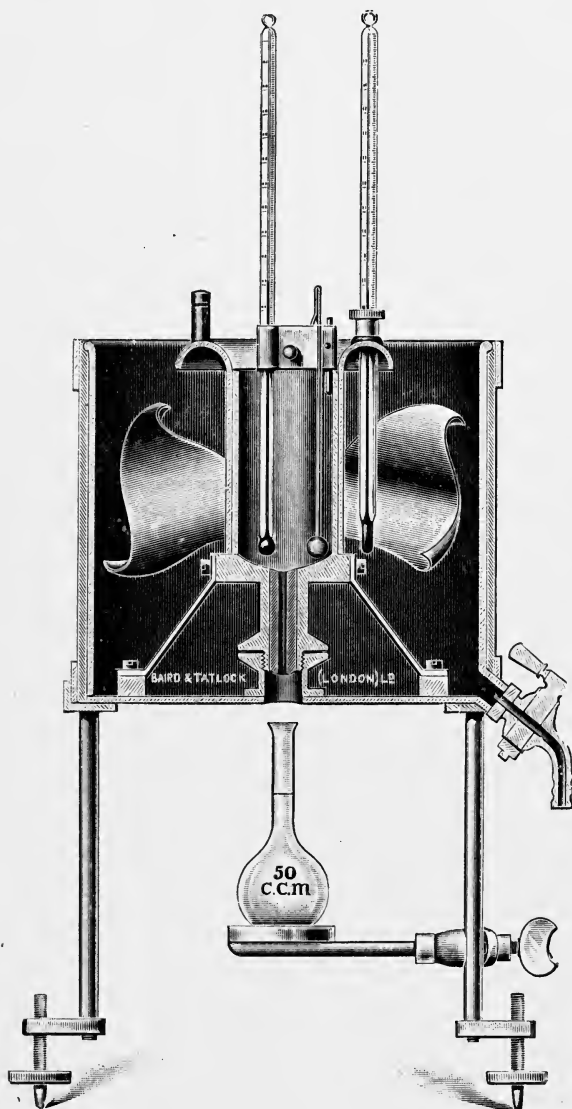


FIG. 23.—Redwood viscometer (section) (Admiralty pattern).

cup, and in such a position that the flow of oil from the orifice will not be interfered with.

The oil-cup is filled with the cooled oil, so that the gauge-point is covered, and the apparatus is then transferred to an efficient ice-chest of suitable design, and the instrument levelled by means of the tripod screws and spirit level provided for that purpose.

As it may be necessary to make more than one test, it will be found desirable to have at least half a pint (about 300 c.c.) of the oil in a stoppered glass bottle placed in the ice-chest with the instrument until required for use. Before commencing a test, the level of the oil in the oil-cup is brought exactly to the point of the gauge. A narrow-necked flask, of 50 cubic centimetres capacity to a mark on the neck, is placed beneath the jet and the ball valve raised and suspended from the thermometer-clip by means of the hook on the stem of the valve, a stop watch being started simultaneously with the lifting of the valve. During the period of testing, the temperature of the oil must remain constant at 32° F. The time of outflow for 50 c.c. is noted and the result given in seconds.

If the oil-cup requires to be wiped out, tissue paper, rather than cloth, should be employed, as filaments of the latter may be left adhering to the surface of the vessel. The agate orifice must not be cleaned with anything which is likely to cause abrasion, and it has been found best to employ twisted tissue paper for the purpose.

A convenient glass instrument is the Coleman-Archbutt viscometer indicated in Fig. 24.

The following description of the apparatus is adapted, by permission, from that given in J. A. Hicks' "Mineral Oil Testing" (C. Griffin).

This instrument is an improved form of the well-known viscometer first used by Coleman about 1869. It consists of a glass pipette contained in an outer jacket, with a funnel for pouring in hot or cold water, a tube for running it off and a stirrer for thoroughly mixing the water in the jacket. The neck at the lower end of the jacket is made narrow and a rubber stopper not more than $\frac{3}{16}$ inch thick is fixed in it; the jet of the efflux tube projects through the stopper only $\frac{3}{16}$ in., and does not extend quite to the end of the neck. Thus the oil in the tube is surrounded by the water in the jacket until it has reached nearly to the end of the jet, and the temperature is maintained constant until the oil has passed out of the tube.

The jet is protected from change of temperature as well

as from fracture by being contained entirely within the neck of the jacket. The efflux tube is narrowed for a short distance above the jet, and four circumferential marks are etched upon it. The lowest or zero mark is rather above the middle of the narrow portion; the other three marks are on the wide portion and divide the tube above the zero mark

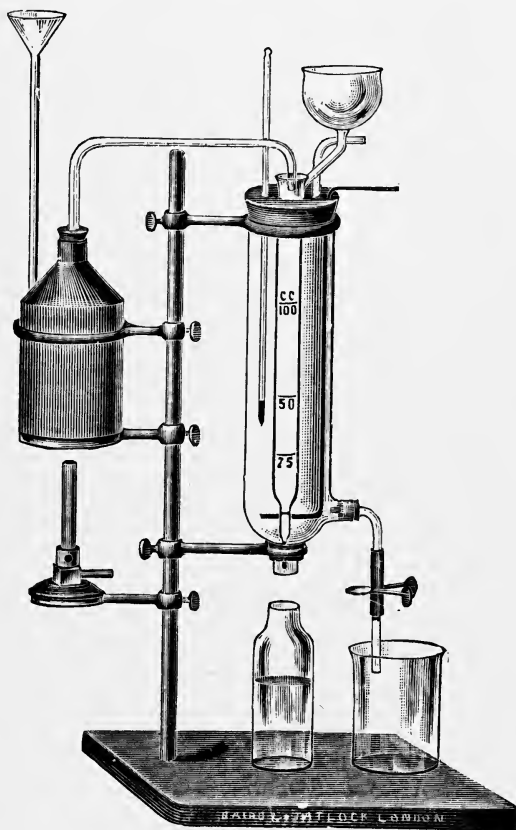


FIG. 24.—Coleman-Archbutt viscometer.

into capacities of 25, 50, and 100 cubic centimetres. The volume of oil used for a test may, therefore, be varied according to the viscosity and the quantity available. The tube must be separately standardized from each mark, as the times of efflux of the different volumes bear no simple relation to each other.

The temperature is maintained constant by pouring hot or

cold water into the jacket, through the funnel, and running off the excess as often as required, using the stirrer frequently. The temperature is indicated by a thermometer immersed in the water. The oil, having been brought to about the desired temperature, is poured into the efflux tube, where the final adjustment is made by stirring with a thermometer, which is removed before the oil is run out. The jet was previously closed by a plug of soft wood, which is now removed and replaced by the finger, and the level of the oil is adjusted exactly to the desired mark. It is then allowed to flow out, and the time occupied in reaching the zero mark is measured by a stop watch, and compared with the time occupied by the standard oil in flowing out under exactly similar circumstances.

When it is desired to make a determination at 212° F., the temperature of the water is gradually raised to about 180° F. by pouring in hot water, and then the funnel is removed and replaced by a tube connected with the metal boiler, and steam is blown in until the water boils. A short bent glass tube is provided for the escape of steam. The length of the jet is about 1 inch, and the diameter is such that 100 cubic centimetres of pure rape oil at 60° F. takes about ten minutes to flow out.

MELTING POINT.

The melting point of a pure substance, like the boiling point, is a perfectly definite temperature, and the purity of a compound is often tested by the sharpness of its melting point.

In the determination of melting points, a small quantity of the finely-powdered substance is placed in a thin walled glass tube, about 1 mm. in diameter, and sealed at one end.

Such tubes are made by softening a test tube in a Bunsen flame and drawing it out to the required diameter. The tube is then broken into lengths of about 6 cms., and one end of each tube is closed by heating in the flame.

Some of the powdered substance is introduced into the open end of one of these tubes, and the tube tapped until the powder is transferred to the bottom to the depth of about 1 cm.

The tube containing the powdered substance is now placed against the thermometer, which has been dipped in the concentrated sulphuric acid contained in a small beaker. Fig. 25A. The tube remains held to the thermometer by capillary attraction.

The thermometer and tube are then supported in the sulphuric acid as shown in the diagram, Fig. 25C. The beaker is heated gradually,* the temperature being allowed to rise slowly, especially near the melting point of the solid. During heating the sulphuric acid is continually stirred by means of a glass rod, as shown in Fig 25B.

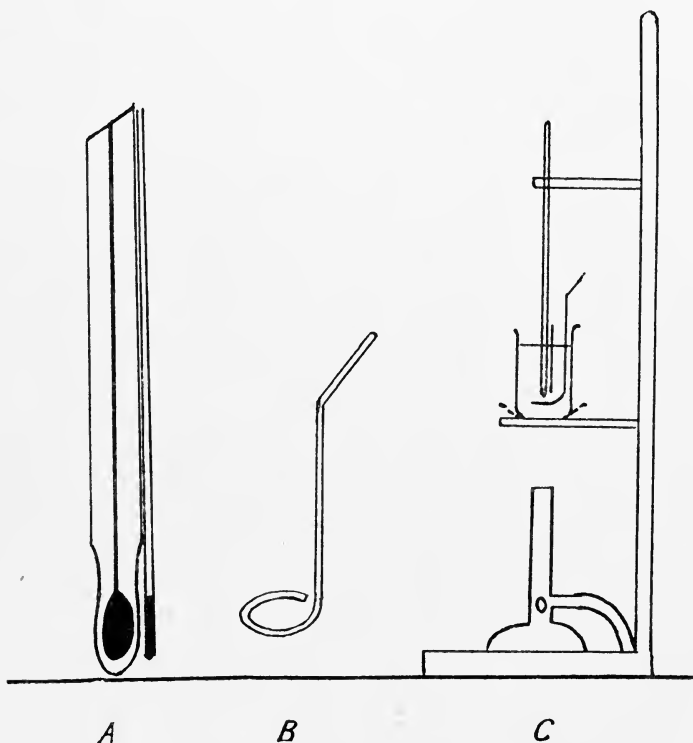


FIG. 25.—Apparatus for determination of melting point.

The temperature at which the solid melts is noted and the process is then repeated with a *fresh sample* of the substance when the sulphuric acid has cooled. If the same sample be used it may be found to melt at a lower temperature than before.

If the sulphuric acid in the beaker becomes dark coloured a small crystal of potassium nitrate should be added, the nitric acid thereby produced oxidizing any impurities present.

If many melting points are to be determined, it is found

* See warning, page 78.

convenient to arrange to work the stirrer by attaching it to a piece of thin string which passes through a glass tube placed above the beaker, and bent twice at right angles.

Stem Correction.—Since the thread of the thermometer extends above the surface of the liquid, in accurate work a correction has to be applied for the difference in temperature between the mercury in the bulb of the thermometer and that in the stem. This applies to all thermometric readings.

If T is the temperature denoted by the thermometer, t the temperature indicated by a thermometer, the bulb of which is midway between the surface of the liquid and the top of the mercury column, the correction to be added =

$$N (T - t) \times 0.000156$$

where N stands for the number of degrees on that part of the thermometer stem containing mercury and not heated by the sulphuric acid, and 0.000156 for the apparent coefficient of expansion of mercury in glass.

DETERMINATION OF THE MELTING POINT OF PARAFFIN WAX (ENGLISH METHOD).

Another method of determining melting points, which is also applicable to the melting point of a complex mixture such as paraffin wax, is to allow some of the fused substance contained in a test tube about 2 cm. diameter, carrying a thermometer and provided with a stirrer, to cool in the air, noting the temperature at which the rapid fall in temperature is arrested. This is best accomplished by taking the temperature every half minute and plotting the results graphically.

Thus in the diagram Fig. 26, the ordinates represent temperatures Centigrade and the abscissæ time in half minutes. In the case of the specimen of paraffin wax (curve A), the initial temperature of the molten wax was 79° C. This fell very rapidly, and the first arrest appeared at a temperature of 54° C. This temperature is registered as the (English) melting point of the wax. Below 54° the temperature of the wax fell *slowly* to 48° when the fall again became more rapid.

The cooling curve for a mixture such as paraffin wax differs in this respect from the curve B, which represents the result obtained under similar conditions with naphthalene.

Here the temperature remained constant at 80° C. until practically complete solidification had taken place, showing that the melting point of naphthalene is 80° C.

The reason for the temperature remaining constant during

solidification is, that in the process of solidification the liquid gives out heat (latent heat of fusion) and this supplies the

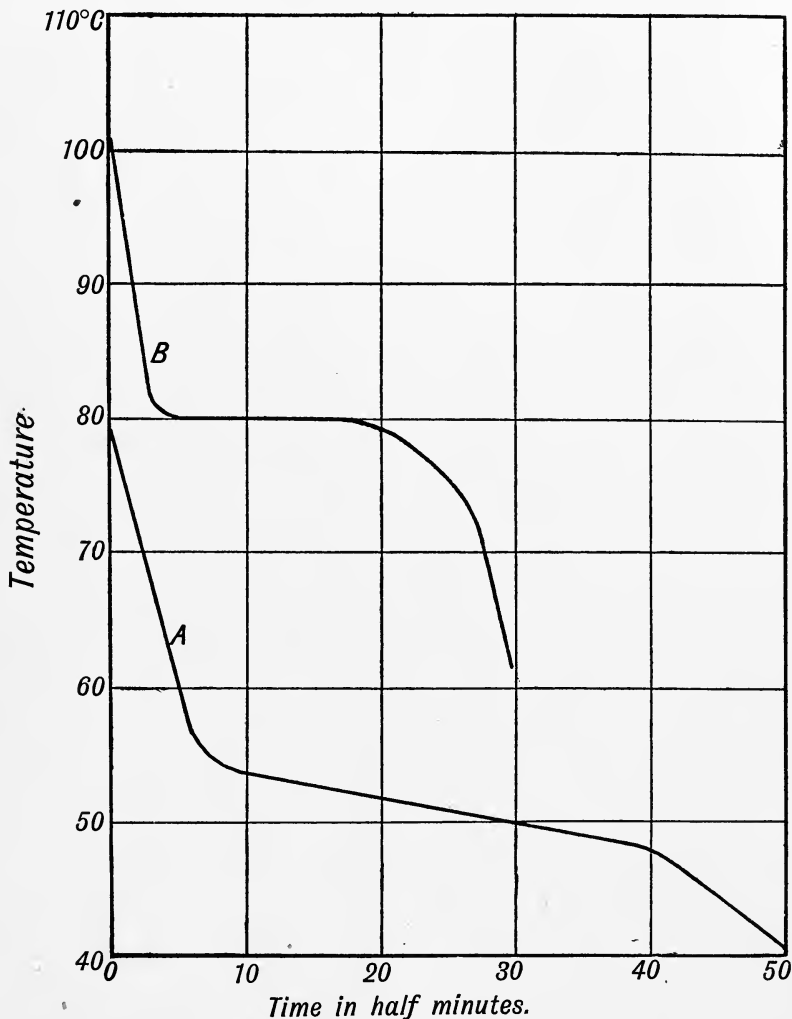


FIG. 26.—Cooling curves of (A) paraffin wax, (B) naphthalene.

heat which is lost by radiation, etc., without causing any fall in temperature of the specimen under examination.

THE MELTING POINT OF PARAFFIN WAX (AMERICAN METHOD).

This melting point test of paraffin wax is carried out by placing the molten sample in a hemispherical dish $3\frac{3}{4}$ inches in diameter, in which is supported a thermometer of which the bulb ($\frac{1}{2}$ inch diameter) is three-quarters immersed.

On cooling a film of wax is produced in patches on the surface, and when this extends to the bulb, the temperature registered is taken as the (American) melting point of the wax.

DETERMINATION OF THE SETTING POINT OF MINERAL OIL.

A boiling tube about 3 cm. diameter is filled with the oil to a depth of about 5 cm. The tube is then cooled in a freezing mixture and slowly stirred by means of a thermometer. After a considerable amount of solid paraffin has separated, the tube is removed from the freezing mixture and the oil constantly stirred until the last trace of solid has disappeared. The temperature at which this occurs is carefully noted and the mean temperature obtained in three determinations is taken as the setting point of the oil.

MELTING POINT OF MIXTURES OF TWO CONSTITUENTS.

It is well known that by dissolving one substance in another, the freezing point of each is depressed, and it will be recalled that this is the principle underlying the determination of molecular weights by the cryoscopic method.

The melting point of mixtures may be investigated by the cooling curve method, employing a bath of liquid for accurate work in order to ensure slow cooling. It is found that if the compositions of mixtures (abscissæ) are plotted against melting points (ordinates) a minimum melting point mixture, known as the eutectic mixture, is obtained, that is, the melting point curve is **V**-shaped.

If, however, the two constituents form a compound, the curve shows two eutectic points and is more or less **W**-shaped, the maximum melting point of the middle portion corresponding to the melting point of the compound, and the composition represented by this point corresponds to the composition of the compound.

For further information on the subject of melting points of

mixtures see Sudborough and James' "Practical Organic Chemistry" (Blackie), pages 22 to 30.

FRACTIONAL CRYSTALLIZATION.

(To be deferred until a later part of the course.)

We must now deal with the methods employed for the separation of the constituents of a solid mixture, when on account of their instability towards heat or for some other reason their partial or complete separation by distillation is impossible.

If one constituent of the mixture be, *e.g.*, an organic acid insoluble in water and the other a solid, neutral substance such as benzophenone $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ or acetanilide $\text{CH}_3\cdot\text{CO}\cdot\text{NHC}_6\text{H}_5$, the acid could of course be removed by shaking the mixture with dilute alkali, the other constituent remaining unchanged and undissolved. It is, however, unnecessary for us to consider such chemical methods of separation; they are dealt with in Chapter XIV.

We shall here concern ourselves solely with those methods of separation which are based on the differing solubilities of various substances in suitable solvents.

The simplest case is the classical example of the mixture of sand and sugar from which the sugar may readily be removed by means of water. In this example the difference in solubility exhibited by the constituents of the mixture is a maximum.

Somewhat less simple would be the separation of a mixture of, *e.g.* potassium chlorate and potassium dichromate, since the solubilities of these salts in water do not differ so much as in the case of sand and sugar.

On boiling up with water a clear solution would be obtained. On allowing to cool a considerable amount of potassium chlorate would be deposited **A** and most of the potassium dichromate together with some of the potassium chlorate would remain in solution. If after filtering off the deposited crystals, the aqueous filtrate M.L.(*a*), or mother liquor, as it is called, were concentrated and then allowed to cool a further quantity of crystals would be thrown down (**X**), but this time the potassium chlorate would be accompanied by a much larger amount of potassium dichromate. If the deposit were filtered off and the mother liquor M.L.(*x*) still further concentrated crystals could be obtained from which potassium chlorate would be almost entirely absent and which would

consist of almost pure potassium dichromate **Y**. The mother liquor from these might be made to yield another deposit **Z**, also consisting of practically pure potassium dichromate.

If now the first deposit **A** were recrystallized from hot water we should obtain almost pure potassium chlorate as deposit **B**. Similarly if the two fractions **Y** and **Z** richest in potassium dichromate were united and dissolved in hot water and quickly cooled, traces of potassium chlorate **P** would be deposited along with the more readily soluble dichromate. This deposit could be filtered off, and on concentration, the filtrate would yield almost pure potassium dichromate **ZZ**. The mother liquors from **Z** and from **ZZ** could if necessary be worked up further if the quantities of potassium dichromate contained therein warranted the time and trouble involved.

Now as regards the intermediate fractions. A description of the methods to be adopted in the purification of the substances contained therein can only be followed if reference be made to the scheme indicated on page 130.

It will be obvious that the substance contained in the mother liquor designated M.L.(*b*) in the scheme will be of approximately the same degree of purity as the crystals **X**, that is, if we assume that sparingly soluble potassium chlorate always tends to separate out and leave an excess of potassium dichromate in the mother liquor.

The reasonable thing to do, therefore, is to dissolve **X** in M.L.(*b*) and to allow the resulting solution to crystallize, yielding deposit **D**, which will now be richer in potassium chlorate than was deposit **X**.

These crystals **D** are now, in fact, of about the same degree of purity as the dissolved matter in M.L.(*c*). They should be dissolved in this mother liquor, giving rise on cooling to deposit **E** which is of sufficient purity to yield practically pure potassium chlorate **F** on recrystallization from water.

Referring to the scheme again it will be seen that the crystals **P** can conveniently be dissolved in M.L.(*Xb*), while the crystals deposited from the solution should be dissolved in M.L.(*Dc*), and so on. Owing to considerations of space and simplicity, however, these operations are not indicated on the scheme.

It is obvious that as the sparingly soluble potassium chlorate is removed from the intermediate fractions and mother liquors the latter will become richer in potassium

EXERCISE IN FRACTIONAL CRYSTALLIZATION.

Separation of a mixture of Acetanilide (M.P. 112°) and Salicylic Acid (M.P. 159°).—[It may be argued that the following detailed account of a complicated and somewhat lengthy process of separation is unnecessary, in view of the fact that salicylic acid, being soluble in dilute sodium carbonate or caustic soda solution, could readily be removed from the mixture, leaving the acetanilide unchanged.

This is of course perfectly true, but the object of the exercise is to illustrate the principles of fractional crystallization, and the two compounds in question were chosen as being readily accessible and comparatively easily soluble in hot water.

If the mixture be made up in large quantities and kept in a stock bottle it is very important that the constituents should be thoroughly mixed, so that portions withdrawn at various times shall not differ appreciably as regards the relative proportions of acetanilide and salicylic acid.]

The melting point of the mixture is first taken, after which fifteen to twenty grams are dissolved by heating with water in a beaker over a wire gauze, the mixture being frequently stirred. It is advisable to commence with an insufficient quantity of water and to add more from time to time till solution is complete, rather than to add a large quantity at the beginning.

This method of procedure should be adopted in all processes of crystallization irrespective of the substance under investigation or the solvent employed. It is manifestly unwise to add at random a quantity of solvent which may be far in excess of that required to form a saturated solution even at room temperature.

When the whole of the mixture has dissolved the clear liquid is allowed to cool to about the ordinary temperature and the crystals which separate are filtered off by means of a Büchner funnel and pump; they must then be washed carefully with a little water which must afterwards be removed as completely as possible by suction and by pressing the crystals with a clean spatula. The liquid from which the crystals have been deposited is known as the mother liquor, and must be carefully preserved. Examination of the crystalline form with a lens or even with the naked eye will readily indicate that the substance is a mixture. Nevertheless its melting point should be taken. To this end a very small portion of the well-pressed crystals is removed and spread out on a

clean fresh piece of porous tile by means of a clean spatula. The last traces of water are in this way removed. The substance should remain on the tile, being occasionally loosened and re-pressed, for fifteen minutes or so before the melting point is taken.

Porous tile must never be employed as a means of removing adhering mother liquor, since some of this would remain on the surface of the crystal, then evaporate, and finally leave a film of impure product on the outside. The mother liquor must always be removed by suction, and as previously stated the crystals must be washed. This applies always, whatever be the nature of the solvent employed. It occasionally, though only rarely, happens that the deposited crystals are so readily soluble in the solvent that the process of washing would entail serious loss. In such cases it would be advisable to dilute the solvent with a certain amount of another liquid in which the crystals would be less soluble and to employ this mixture for washing purposes.

After the melting point has been taken, all the crystals, which may be called the first deposit, are dissolved in hot water under the same conditions as before, and the crystals which separate on cooling are filtered off and washed. A very small portion of this second deposit is dried on tile and the melting point taken. (Does it melt any higher than the first deposit or the original mixture?) The mother liquor is set aside as before and may be labelled "Mother liquor from second crystallization of original substance."

The substance is now recrystallized twice more, the melting point being taken each time. After these four crystallizations the product should consist almost exclusively of the long needle-shaped crystals of salicylic acid. One more recrystallization will probably yield a perfectly pure specimen. This fifth deposit may conveniently be known as the most sparingly soluble fraction.

We have now carried out five crystallizations and shall therefore have five mother liquors, of which that from the first crystallization of the original mixture will usually contain the largest percentage of the more soluble acetanilide. (The mother liquor from the fifth crystallization will obviously be an almost pure solution of salicylic acid.)

The mother liquor from the first crystallization should be concentrated somewhat by evaporation on the water bath, and the melting point of the crystals which separate on cooling should be determined and these crystals should then be recrystallized from a fresh quantity of water. The deposit

obtained on cooling will probably be small in quantity but may consist of almost pure acetanilide. If the melting point indicate that it still contains some of the sparingly soluble substance it should be set aside till a further quantity of substance of a similar degree of purity be obtained, when the whole may again be recrystallized.

The intermediate mother liquors which contain considerable quantities both of acetanilide and of salicylic acid should now be worked up.

It may here be mentioned that the deposition of crystals from solutions may frequently be effected by the addition of a small crystal of the dissolved substance and by rubbing the sides of the containing vessel with a glass rod. Frequently this last device is successful even without the first.

Suppose one of the intermediate mother liquors, say that from the second crystallization of the original mixture, has deposited crystals on standing. These will almost certainly contain both components. They should be filtered off and dissolved in the mother liquor from the third crystallization, that is, the next mother liquor which contains a rather higher percentage of the more sparingly soluble substance.

The solution is then allowed to crystallize and the substance deposited should contain a higher percentage of salicylic acid than that which had just been dissolved. By dissolving this new fraction in the mother liquor from the fourth crystallization and allowing to crystallize a still purer specimen of salicylic acid can be obtained. This is then made to pass through the fifth mother liquor, when it should be practically pure and can be added to the pure salicylic acid previously separated. Each operation should be checked by melting point determinations.

One or two successive intermediate fractions may now be united and concentrated somewhat, the volume of the solution being adjusted so that only a small quantity of solid crystallizes out on cooling.* This is removed, the filtrate concentrated to a much smaller bulk and the deposit which separates on cooling is filtered off, examined with a lens and the melting point determined.

These crystals may then be dissolved in the *next* mother liquor containing a more readily soluble fraction, *i.e.* the nearest mother liquor which contains a higher percentage of acetanilide. A small amount of solid is allowed to separate,* after which

* These two deposits will probably contain relatively large amounts of salicylic acid; if their M.P. indicate this they may be passed through mother liquors rich in that substance.

the remaining mother liquor may be further concentrated and made to yield a deposit rich in acetanilide.

Determination of the melting point must decide whether this deposit should be set aside as practically pure or whether it should be passed through another and still "lower" mother liquor, *i.e.* one containing a still greater proportion of acetanilide.

The isolation of a considerable quantity of acetanilide, or in general of the more readily soluble component of any mixture in a pure condition by means of fractional crystallization, is always somewhat difficult.

Although in working through the various fractions in order to obtain more of the pure sparingly soluble substance it is customary to place a given fraction in the next higher mother liquor and to cause the solution to crystallize, in the hope that the resulting deposit will be purer, this method should not be blindly followed, but should be checked by the determination of melting points, otherwise much time and labour will be wasted.

It occasionally happens that when a substance is being purified by repeated crystallization, an intermediate fraction may be obtained, which, owing to special or even accidental conditions of crystallization, is found to be practically pure.

In such a case it would obviously be unwise (as tending only to re-contaminate the product) to dissolve it in the next higher mother liquor. It should be set aside till a further quantity of a similar degree of purity is obtained, when both should be united and recrystallized from pure water, or from a mother liquor containing the sparingly soluble substance in a practically pure condition.

These remarks apply equally well to the operations which are carried out with the object of isolating the readily soluble component in a pure condition.

It may be mentioned in conclusion that there are few operations in chemistry the success of which depends more upon what may be called the personal equation of the manipulator than does that of fractional crystallization, although there are numerous other operations, such as fractional distillation, gas manipulations, and the estimation of carbon, hydrogen and nitrogen by the process known as "combustion," into which this equation enters largely.

In order that the process of fractional crystallization may be carried out successfully, it is essential that all the apparatus employed, such as beakers, funnels, filter flasks, glass rods for stirring, as well as spatulas, should be scrupulously clean.

Great care must also be taken to guard against the common error of employing large flasks, funnels, etc., for the manipulation of very small quantities of liquids or of crystals, since this leads to considerable loss of material.

Lipped beakers should always be employed for crystallizations, except in case of *very* volatile solvents, when conical flasks may be used. The use of the so-called "crystallizing dishes" is to be deprecated almost invariably.

CHAPTER VII

VAPOUR DENSITY AND ALLIED PROBLEMS

As explained on page 109, the densities of solids and liquids are referred to water at a definite temperature as a standard. In the case of gases and vapours * this substance is unsuitable for the purpose, since its adoption would necessitate such small fractional values for their densities. On this account hydrogen, the lightest known substance, is taken as the standard to which the densities of gases and vapours are referred.

As in the case of solids and liquids, the vapour density of a substance is equal to the weight of a certain volume of the gas or vapour divided by the weight of an equal volume of the standard substance. It is, however, extremely important in this case to specify that the gas or vapour and the hydrogen must be measured at the same temperature and pressure, since these considerations exert such a marked influence on the volume of a gas. By means of this definition of vapour density and by applying Avogadro's Hypothesis, it is possible to show the relation which exists between the vapour density of a substance and its molecular weight in the state of vapour. Thus—

$$\text{Vapour density} = \frac{\text{weight of a certain volume of gas or vapour}}{\text{weight of an equal volume of hydrogen at the same temperature and pressure}}$$

In these equal volumes of gas or vapour and hydrogen at the same temperature and pressure, there are an equal number of molecules (Avogadro's Hypothesis).

$$\therefore \text{V.D.} = \frac{\text{weight of "n" molecules of gas or vapour}}{\text{weight of "n" molecules of hydrogen}}$$

$$\therefore \text{V.D.} = \frac{\text{weight of one molecule of gas or vapour}}{\text{weight of one molecule of hydrogen}}$$

* For the distinction between the terms *gas* and *vapour*, see page 145.

$$\therefore \text{V.D.} = \frac{\text{molecular weight of the substance in the state of vapour}}{\text{molecular weight of hydrogen}}$$

$$\therefore \text{V.D.} = \frac{\text{M.W.}}{2}$$

or the molecular weight of a substance in the state of vapour is equal to twice its vapour density.

(The reasons for assigning the value 2 for the molecular weight of hydrogen are as follows :—

It is found by experiment that one volume of hydrogen + one volume of chlorine give two volumes of hydrogen chloride gas, provided that all the gases are measured at the same temperature and pressure. Whence it follows by Avogadro's Hypothesis, n molecules of hydrogen + n molecules of chlorine give $2n$ molecules of hydrogen chloride, or 1 mol. hydrogen + 1 mol. chlorine = 2 mols. hydrogen chloride.

No case is known where one *volume* of hydrogen gives rise to more than two *volumes* of a compound, from which it follows that one *molecule* of hydrogen never produces more than two *molecules* of a compound. Hence one molecule of hydrogen is never known to give more than two *atoms* of hydrogen. In other words, the molecule of hydrogen is regarded as containing two atoms. The weight of an atom of hydrogen is taken as unity, and it follows that the weight of a molecule of hydrogen is equal to 2.)

In some cases the vapour density of a substance is referred to air as a standard. The density of air is 14.4 ($H = 1$); hence if the density of a substance is referred to air, its density compared with hydrogen will be this value multiplied by 14.4.

(The density of air is determined by experiment, but it may be arrived at by calculation as follows :—

100 volumes of air contain approximately 80 volumes of nitrogen and 20 volumes of oxygen. The density of nitrogen is 14 and of oxygen 16 [$H = 1$].

		Volumes of hydrogen.
80 volumes of nitrogen are as heavy as	80 × 14 = 1120	
20 " oxygen " "	20 × 16 = 320	
—		
∴ 100 " air " "	1120 + 320 = 1440	
∴ 1 volume of air is as heavy as 14.4 volumes of hydrogen, or the density of air = 14.4 [$H = 1$]).		

The experimental determination of the vapour density of a substance is a comparatively simple matter.

In the case of substances which are gaseous under ordinary conditions, it is only necessary to compare the weights of equal volumes of the gas and of hydrogen under the same conditions of temperature and pressure. The experimental details are described in books on Inorganic Chemistry.

In the case of substances which are liquid under ordinary conditions, one of three well-known methods, those of Hofmann, Victor Meyer, or Dumas may be employed. The method of Victor Meyer will be described.

In the expression—

$$\text{V.D.} = \frac{\text{weight of a certain volume of vapour}}{\text{weight of an equal volume of hydrogen at the same temperature and pressure}}$$

the weight of the vapour is obviously equal to the weight of the liquid employed for the experiment.

In order then to determine the vapour density of a substance it would appear to be necessary to vaporize a certain weight of liquid and find by calculation the weight of a volume of hydrogen equal to this volume of vapour under the same conditions of temperature and pressure.

In the Victor Meyer method the determination is carried out by means of an apparatus as shown in the diagram Fig. 27.

In the outer vessel A a liquid of boiling point some 40° higher than that of the substance of which the vapour density is to be determined, is placed and allowed to boil throughout the experiment, some pieces of porous tile having previously been placed in A.

In the case of substances such as ether and very light hydrocarbons, water is quite suitable for this purpose, but in the determination of the vapour densities of substances of higher boiling point, a liquid such as xylene, B.P. 140° or aniline, B.P. 183°, etc., should be employed.

On heating the liquid in A, air is expelled owing to expansion from the inner tube B, which is closed at C by means of a rubber stopper. The end of the side tube D dips into a trough E containing water.

When no more air escapes, a graduated tube F filled with water is inverted over D.

A weighed quantity of the liquid in a small stoppered bottle H (Hofmann bottle) is now introduced into the tube B, by removing the stopper at C momentarily. The stopper of

the Hofmann bottle is forced out owing to expansion, and the liquid evaporates. A volume of *air* at the temperature of the tube B, equal to the volume of vapour produced, is displaced and passes out of B into the graduated tube F. This air on passing through the water is cooled, and consequently the volume collected over water is less than the volume of hot vapour produced, but is equal to the volume which the vapour

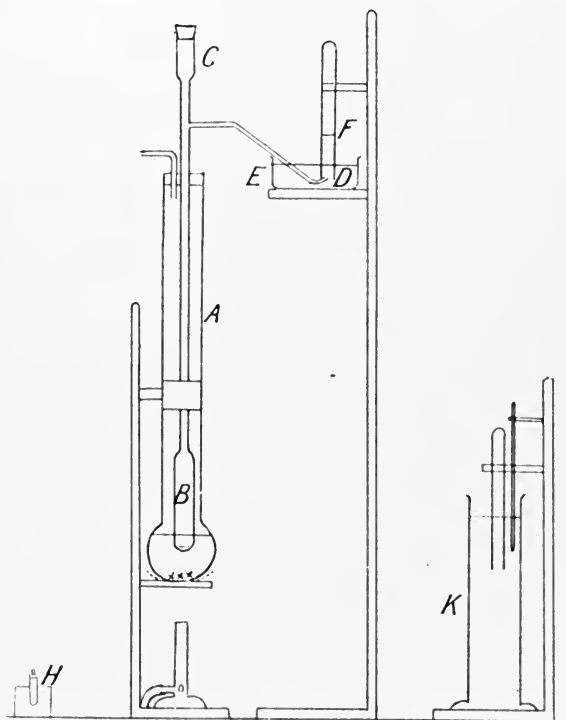


FIG. 27.—Victor Meyer's apparatus for determining vapour densities.

would occupy, if it could exist in the state of vapour under the conditions of the experiment.

It is important to notice that it is displaced air which is collected and *not* vapour, otherwise if vapour passed out of the tube B, it would condense in the water and the determination be vitiated.

For this reason it is of importance that the tube B should be perfectly dry before starting an experiment, as if water vapour is displaced from B it will likewise condense.

When no more air escapes through D, the tube F is slightly

raised, so as to free it from D, care being taken that it is not lifted out of the water. A crucible filled with water is now placed in the trough E, and the end of the tube F inserted in it. By this means the tube F and contents may be transferred to a tall cylinder K, which has been previously filled with water and allowed to stand so as to attain the room temperature. The crucible is removed when the end of the tube is under the surface of the water in the cylinder. The height of the tube F in the cylinder is adjusted until the level of the water inside is the same as that outside. The tube E is then supported by means of a clamp and allowed to stand for a quarter of an hour.

Finally, the height of the tube is adjusted and the volume of the air enclosed is noted.

This air is measured at the temperature of the room and at atmospheric pressure, since the level of the water outside and inside is the same. As previously explained, if the vapour of the given weight of liquid under examination did not condense on cooling, its volume at this temperature and pressure would be the same as that of the air collected.

The temperature and pressure at which the relation between the weight and volume of hydrogen is known, is 0° C. and 760 mm. pressure, denoted N.T.P. The volume of air displaced must therefore be reduced to this temperature and pressure.

We can then find by calculation the weight of a volume of *hydrogen* equal to this corrected volume of air, and thus have all the data necessary for the calculation of the vapour density of the liquid.

The air contained in the tube F is saturated with water vapour. The sum of the pressures exerted by the air and water vapour is equal to the atmospheric pressure, which is obtained by reading the barometer. The pressure of saturated aqueous vapour at the room temperature is obtained from tables, so that the pressure exerted by the air, which is the difference of these two pressures, is found.

From the relation 2 grams of hydrogen occupy 22.4 litres (or 1 cc. = 0.00009 gram) at 0° and 760 mm., the weight of the volume of hydrogen equal to the volume of the displaced air, corrected to N.T.P., is calculated, and hence the vapour-density of the liquid is found.

Before commencing an experiment, dry the tube B by drawing air through it by means of a long glass tube attached to a water pump, and by gently heating it over a Bunsen flame. Place a small quantity of sand, which has been

previously heated, in the tube B to break the fall of the Hoffmann bottle.

Suppose in a particular experiment :

Weight of Hoffmann bottle empty . .	2.1350 gram
" " " + ether . .	2.2293 "
<hr/>	
Weight of ether . .	0.0943 "
<hr/>	

Volume of air displaced, 32.2 c.c.

Measured at 15° C.

Atmospheric pressure = 753 mm.

Tension of aqueous vapour at 15° = 13 mm.

∴ Pressure of dry air = 740 mm.

Volume of air displaced at 0° and 760

$$= 32.2 \times \frac{760}{740} \times \frac{273}{288}$$

$$= 29.7$$

Weight of hydrogen equal to this volume of air

$$= 29.7 \times 0.00009 \text{ grams}$$

$$= 0.002573 \text{ gram}$$

$$\text{Vapour density of ether} = \frac{0.0943}{0.002573} = 37.5$$

$$\therefore \text{Molecular weight} = 75$$

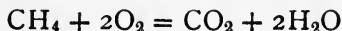
VOLUME RELATIONS OF GASES AND VAPOURS.

It follows from Avogadro's Hypothesis that if two grams of hydrogen (1 gram molecule) occupies 22.4 litres at 0° and 760 mm., a gram molecule of any other gas or vapour will occupy the same volume, under the same conditions of temperature and pressure. Or, as has just been shown in connexion with vapour density, the weights of equal volumes of gases under the same conditions of temperature and pressure are proportional to the molecular weights of the substances.

The application of this principle is, of course, of the utmost importance in all calculations relating to volumes of gases and vapours.

Thus, suppose it is required to find the volume of air required for the complete combustion of 1 cubic foot of methane.

From the equation—



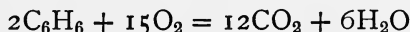
1 gram molecule of methane requires 2 gram molecules of

oxygen; or 22.4 l. of methane at 0° and 760 mm. requires 2×22.4 l. of oxygen at the same temperature and pressure; or 1 vol. methane at any temperature and pressure requires 2 vols. oxygen at the same temperature and pressure.

\therefore 1 cubic foot of methane at any temperature and pressure requires 2 cubic feet of oxygen. But $\frac{1}{5}$ th air by volume is oxygen.

\therefore 10 cubic feet of air would be required, both gases being measured at the same temperature and pressure.

The relation between volumes of gram molecules (gram molecular volumes) holds good, of course, only for gases and vapours and not for liquids and solids. For example, a calculation might be made to find the volume of benzene vapour produced from one gram of benzene at 200° C. and 750 mm., the volume of air required for its complete combustion, and the volume of carbon dioxide and water vapour produced. From the equation—



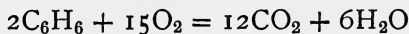
2 gram molecules or 2×78 grams of benzene would produce 2×22.4 litres of benzene vapour at 0° and 760 mm., if the vapour could exist under such conditions.

At this temperature and pressure, however, the benzene would not be present solely as vapour—most of it would be solidified, since the M.P. of benzene is 6° C.—but at the temperature given above, *i.e.* 200° and at 750 mm., it would be completely in the vaporous condition and would obey the gas laws.

Thus 156 grams benzene should produce 44.8 l. of vapour at 0° C. and 760 mm.

Or 1 gram benzene should produce $\frac{44.8}{156} = 0.287$ l. at 0° C. and 760 mm. At 200° C. and 750 mm., this would occupy $0.287 \times \frac{473}{273} \times \frac{760}{750} = 0.504$ l.

Also from the equation—



it follows that 2×78 grams benzene require 15×22.4 litres of oxygen and produce 12×22.4 litres CO_2 at N.T.P. Since the gases are measured above 100° C. and at a pressure not greater than 760 mm., the water produced will all be in the state of vapour.

6 × 22.4 litres of water vapour should be produced at 0° and 760 mm.

It follows from the above equation that at 200° C. and 750 mm. or at any temperature slightly above the boiling point of water (the substance having the highest boiling point of the four substances considered), *two* volumes of benzene vapour require *fifteen* volumes of oxygen and produce *twelve* volumes of carbon dioxide and *six* volumes of steam.

It has been shown above that at 200° C. and 750 mm. 1 gram. of benzene produces 0.504 litre of benzene vapour.

∴ 0.504 litre of benzene vapour requires $0.504 \times \frac{15}{2} = 3.88$ litres of oxygen and produces $0.504 \times \frac{12}{2} = 3.024$ litres of carbon dioxide and $0.504 \times \frac{6}{2} = 1.512$ litres of steam, all the substances being measured at 200° C. and 750 mm. pressure.

∴ Volume of air required for complete combustion = $3.88 \times 5 = 19.4$ litres at 200° C. and 750 mm.

Another important problem on volume relations of gases is met with in determining the formula of a *gaseous* hydrocarbon from the results obtained on its combustion in oxygen.

Thus, 10 c.c. of a *gaseous* hydrocarbon were mixed with 55 c.c. of oxygen and the mixture exploded.

After explosion the volume of the residual gases was 35 c.c., of which 30 c.c. were absorbed by potassium hydroxide solution and the remaining 5 c.c. by a solution of pyrogallol containing potassium hydroxide. All the gases were measured at the ordinary atmospheric temperature and pressure. What is the molecular formula of the hydrocarbon?

Since 30 c.c. of the gaseous product of the reaction are absorbed by a solution of potassium hydroxide, this is the volume of carbon dioxide produced; the remaining 5 c.c. is excess of oxygen. The volume of water produced may be neglected (see below).

∴ 10 c.c. original gaseous hydrocarbon produce 30 c.c. carbon dioxide; or 1 vol. gaseous hydrocarbon produces 3 volumes carbon dioxide.

From Avogadro's Hypothesis it follows that 1 molecule gaseous hydrocarbon produces 1 molecule carbon dioxide. But one molecule of carbon dioxide contains one atom of carbon; or 3 molecules of carbon dioxide contain 3 atoms of carbon.

∴ 1 molecule of original hydrocarbon contains 3 atoms of carbon; or formula of hydrocarbon is C_3H_x .

To find the number of atoms of hydrogen in the molecule

we have to find what volume of oxygen is used for combination with the hydrogen in the 10 c.c. of hydrocarbon gas used in the experiment.

The total volume of oxygen used is obviously equal to the volume of oxygen originally taken minus the excess found at the end of the experiment = $55 - 5 = 50$ c.c.

The oxygen used for the combustion of the hydrogen is equal to the total oxygen used minus that used for the combustion of the carbon.

The oxygen used for the carbon is equal to the volume of carbon dioxide produced (1 volume of carbon dioxide contains its own volume of oxygen). Volume of carbon dioxide produced = 30 c.c.

\therefore Volume of oxygen used for hydrogen = $50 - 30 = 20$ c.c. (since total oxygen used is 50 c.c.). But 1 volume of oxygen unites with 2 volumes of hydrogen, or 20 c.c. oxygen combine with 40 c.c. hydrogen.

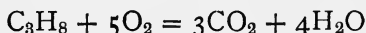
\therefore 40 c.c. of hydrogen must have been produced from 10 c.c. of original hydrocarbon, hence 10 c.c. hydrocarbon gas give 40 c.c. hydrogen,

\therefore 1 volume hydrocarbon gas gives 4 volumes hydrogen,

\therefore 1 molecule hydrocarbon gas gives 4 molecules of hydrogen; four molecules of hydrogen = $4\text{H}_2 = 8\text{H}$.

\therefore 1 molecule of the hydrocarbon contains *three* atoms of carbon and *eight* atoms of hydrogen, or C_3H_8 is the formula required.

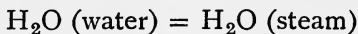
This is confirmed as follows :—



22.4 l. require 5×22.4 l. oxygen and produce 3×22.4 l. of carbon dioxide, or 1 vol. requires 5 vols. oxygen and produces 3 volumes of carbon dioxide ;

\therefore 10 c.c. would require 50 c.c. of oxygen and produce 30 c.c. of carbon dioxide, which is what is found by experiment.

It will be noticed that in the above example the amount of water produced is neglected. Since all the gases are measured at the ordinary temperature, the water vapour condenses, and the volume of liquid water produced is negligible. Thus from the equation



18 grams of water should give 22.4 l. of water vapour at 0° and 760 mm., that is 1 c.c. of water would give more than one thousand times its own volume of water vapour, hence

the volume of liquid water obtained on condensation is negligible.

It will be obvious that the above method of calculating the molecular formula of a hydrocarbon is only applicable to substances in the gaseous or vaporous condition, since, as previously explained, the gram molecular volume relation only holds for gases and vapours.

Further calculations involving volume relations of gases and vapours will be found on page 334.

THE DIFFERENCE BETWEEN A GAS AND A VAPOUR.

It has been found in connexion with the liquefaction of gases that for every substance there exists a particular temperature, called the *critical* temperature, above which the gas cannot be liquefied by the application of pressure alone.

The critical temperatures of some of the commoner substances are as follows :—

Hydrogen	-241° C.
Oxygen	-119°
Carbon dioxide	+ 31°
Sulphur dioxide	+155°
Benzene	+287°
Water	+358°

Strictly speaking, gaseous material should only be called a gas when it is at a temperature above its critical temperature ; at all temperatures below this it should be called a vapour.

We speak of carbon dioxide and sulphur dioxide *gases*, but at ordinary temperatures these substances are in reality vapours, since their critical temperatures are 31° C. and 155° C. respectively. On the other hand, water exists as a gas only above 358° C.

CHAPTER VIII

FLASH POINT

THE flash point of an oil is the lowest temperature at which sufficient vapour is given off to ignite momentarily on the introduction of a spark or flame.

The flash point is dependent on the vapour pressure of the oil and on the percentage of oil vapour necessary to produce an explosive mixture with air.

For this reason it is obvious that the flash point registered will be lower if the vapour of the oil is allowed to accumulate in a closed vessel, than if it escapes from an open vessel. On this account the terms *closed* and *open* test flash points are employed. The former flash point determination, however, being much more reliable, is of considerably greater importance.

The Closed Test Flash Point.—To obtain comparable results, it is necessary to employ always the same standard apparatus, since the form of apparatus used has an important influence on the temperature at which the oil “flashes.”

The closed test flash point for illuminating oils is fixed by law at not lower than 73° F., using the standard apparatus described below. This temperature was adopted since it was found that a closed test flash point of 73° F. corresponds to an open test flash point of 100° F. This was the legal limit for the flash point previous to the year 1879; the open flash test being the one exclusively employed previous to this date.

The apparatus* legally recognized and usually employed in this country is that known as the Abel flash point apparatus, represented in Fig. 28. (See also Fig. 29.)

It consists of a cylindrical oil-cup 2 inches in diameter and 2.2 inches deep, and which is filled to the point of the gauge ($1\frac{1}{2}$ inches from the bottom) with the sample to be tested, or if the sample of oil is insufficient the cup may previously be partly filled with water.

An air space half an inch across surrounds this cup, and

* The description of this apparatus is adapted, by permission, from that given in J. A. Hicks' "Mineral Oil Testing" (C. Griffin).



FIG. 28.—Abel flash point apparatus.

heat passes to the oil through this air space from the water contained in the outer jacket. A small colza oil or coal gas test lamp is fitted to a movable slide on the cover of the cup, and is so arranged that the flame is directed downwards when the slide is moved to open the cup.

The following details as to working are taken from the

PETROLEUM ACT, 1879 (42 & 43 Vict. c. 47).

"MODE OF TESTING PETROLEUM SO AS TO ASCERTAIN THE TEMPERATURE AT WHICH IT WILL GIVE OFF INFLAMMABLE VAPOUR.

"The test apparatus should be placed for use in a position where it is not exposed to currents of air or draughts.

"The heating vessel or water bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F., and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

"If the water has been heated above the required temperature, it is easily cooled to 130 degrees by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

"When a test has been completed the temperature of water in the outer jacket is again raised to 130 degrees by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh supply to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

"The test lamp is prepared for use by fitting it with a piece of flat plaited candle-wick* and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube.

"The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch in diameter,† and this size of flame is

* The description of wick known as Field's night-light candle-wick has been found most suitable.

† The size of the small ivory ball on the lid.

readily maintained by simple manipulation from time to time with a small wire trimmer.

"When gas is available it may conveniently be used in place of the little oil lamp, and for this purpose a test flame arrangement for use with gas has been devised, which may be substituted for the lamp.

"The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° F., the samples to be tested should be cooled down (to about 60 degrees) by immersing the bottles containing them in cold water, or by any other convenient method.

"The lid of the cup, with the slide closed, is then put on, and the cup is placed in the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered.

"When the cup has been placed in a proper position, the scale of the thermometer faces the operator.

"The test lamp is then placed in position upon the lid of the cup, the lead line or pendulum * which has been fixed in a convenient position in front of the operator is set in motion, and the rise of the thermometer in the petroleum cup is watched.

"When the temperature has reached about 66 degrees the operation of testing is to be commenced, the test flame being applied once for every rise of one degree in the following manner :—

"The slide is slowly drawn open while the pendulum performs *three* oscillations, and is closed during the *fourth* oscillation.†

"*Note.*—If it is desired to employ the test apparatus to determine the flashing points of readily volatile oils, the mode of procedure is to be modified as follows :—

"The air chamber which surrounds the cup is filled with *cold* water, to a depth of 1½ in., and the heating vessel or water bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus and kept there during the

* Pendulum 24 inches long.

† *One* oscillation is taken to mean the movement in one direction only ; the complete oscillation backwards and forwards is for this purpose regarded as *two* oscillations.

entire operation. If a heavy oil is being dealt with, the operation may be commenced with water previously heated to 120 degrees instead of with cold water."

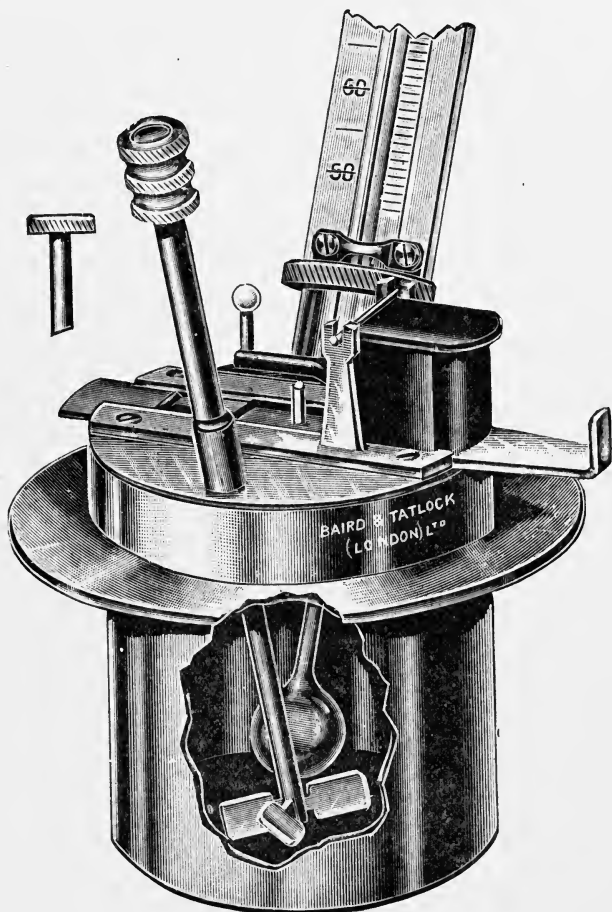


FIG. 29.—Modified Abel flash point apparatus.

A modified form of Abel apparatus* is shown in Fig. 29, in which a rotating stirrer is employed.

Legal recognition was given to this arrangement by an Order in Council, May, 1907 (Statutory Rules and Orders 1907, No. 483), wherein the method of using the instrument is described as follows:—

* See also J. A. Hicks' "Mineral Oil Testing" (C. Griffin).

"1.—LIQUID MIXTURES.

"Where the petroleum mixture is wholly liquid, flows quite freely, and does not contain any sediment or thickening ingredient, such mixture shall be tested in the manner set forth in Schedule I. to the Petroleum Act, 1879.*

"2.—VISCOUS AND SEDIMENTARY MIXTURES.

"Where the petroleum mixture contains an undissolved sediment, as in the case of some metal polishes, which can be separated by filtration or by settlement and decantation, the sediment may be so separated and the decanted liquid may be tested in the manner set forth in Schedule I. to the Petroleum Act, 1879.

"In carrying out such separation, care must be taken to minimize the evaporation of the petroleum. The separation of the sediment must not be effected by distillation.

"Where the petroleum mixture is such that sediment cannot be separated by the aforementioned means, or where it is of a viscous nature, as in the case of indiarubber solution, quick-drying paints, etc., such mixture shall be tested in the apparatus modified as shown in the drawing hereto. This apparatus differs from that prescribed in Schedule I. to the Petroleum Act, 1879, only in the addition of a stirrer to equalize the temperature throughout the sample under test.

"In carrying out the test of a viscous petroleum mixture, this stirrer shall be constantly revolved at a slow speed except when applying the test flame, the direction of revolution being that of the hand of a clock.

"With the exception of the use of the stirrer, the manner of carrying out the test shall be that set forth in Schedule I. to the Petroleum Act, 1879.

"The stirrer may be removed by grasping the spindle just above the blades with the finger and thumb, and unscrewing the upper sheath. The opening in the lid, through which the stirrer passes, may then be closed by a plug provided for the purpose.

"When this has been done, the apparatus shall be deemed to comply with the specification set forth in Schedule I. of the Petroleum Act, 1879, and may be used for testing ordinary petroleum or solid petroleum mixtures.

"A model of the aforementioned apparatus is deposited with the Board of Trade, and the provisions of Section 3 of

* By means of the apparatus described on page 146.

the Petroleum Act, 1879, in regard to verification and stamping shall apply also to such apparatus as though it were the apparatus prescribed by the said Act.

"For the purpose of carrying out such verification the stirrer shall be removed and the opening plugged as hereinbefore directed. The apparatus shall then be tested with ordinary petroleum.

"3.—SOLID PETROLEUM MIXTURES.

"Where the petroleum mixture is solid, as in the case of naphtha soaps, etc., the apparatus to be used for the test shall be that prescribed in Schedule I. of the Petroleum Act, 1879.*

"The method of carrying out the test of such solid mixture shall be as follows:—

"The solid mixture must be cut into cylinders $1\frac{1}{2}$ in. long and $\frac{1}{4}$ in. in diameter by means of a cork borer or other cylindrical cutter having the correct internal diameter. These cylinders are to be placed in the petroleum cup of the testing apparatus in a vertical position in such number as will completely fill the cup. The cylinders must be in contact with one another, but must not be so tightly packed as to be deformed in shape.

"Five or six of the cylinders in the centre of the cup must be shortened to $\frac{1}{2}$ in. to allow space for the thermometer bulb.

"The air bath of the testing apparatus must be filled to a depth of $1\frac{1}{2}$ in. with water. The water bath must then be raised to and maintained at a temperature of about 75° F.

"The cup must then be placed in the air bath, and the temperature of the sample must be allowed to rise until the thermometer in the oil cup shows 72° F., when the test flame must be applied.

"If no flash is obtained the temperature must be maintained constant in the oil cup for one hour, at the expiration of which the test flame must again be applied.

"If a flash is obtained, the solid mixture will be subjected to the provisions of the Petroleum Acts in virtue of this Order.

"*Note.*—It may in many cases save time in testing samples of petroleum mixtures to apply the test flame after

* By means of the apparatus described on p. 146.

the sample has been a few minutes in the cup and while still at the temperature of the room in which the test is being carried out, provided that this temperature is below 73°F . If a flash is obtained by this means, it is unnecessary to proceed with the test at a higher temperature."

Various other forms of flash point apparatus are in use. For example, in Germany, to avoid the personal error likely to be introduced in opening the slide, a clockwork movement is adopted, the apparatus being known as the Abel-Pensky Petroleum Tester.

For descriptions of other forms of apparatus see J. A. Hicks' "Mineral Oil Testing" (Griffin).

Effect of Pressure on Flash Point.—For accurate work it is necessary to correct the observed flash point for atmospheric pressure, since if the pressure is low the flash point will be lower than if the atmospheric pressure is high; that is, in the former case the liquid more readily evaporates than in the latter.

A difference of 1 inch in the height of the barometer corresponds to 1.6°F . in the flash point. For the sake of uniformity, flash points should be corrected to a pressure of 30 inches of mercury.

Thus, if the flash point of an oil is 70°F . when the height of the barometer is 28 inches, its flash point at 30 inches pressure would be $70 + 2 \times 1.6 = 73.2^{\circ}\text{F}$. A table for the correction of flash points in degrees Centigrade to a pressure of 760 mm. is given in Thomson, Redwood and Cooper-Key's "Handbook on Petroleum" (Griffin), p. 100.

The Open Test Flash Point and Fire Test.—If the oil be heated in an *open* vessel the temperature at which a flash occurs on applying a light to the vapour will be higher than in the "closed" test, since in this case the vapour is not allowed to accumulate.

For various reasons the "open" test is not so reliable as the "closed" test. However, it is often of value in the case of heavy oils.

To carry out the "*open*" flash test, the oil may be heated in the ordinary flash point apparatus with the lid removed, or in a porcelain crucible placed through a hole in a sheet of asbestos, a thermometer being suspended in the oil so that the top of its bulb is about $\frac{1}{4}$ inch below the surface.

The oil is heated at the rate of 10°F . per minute, and a small free flame, such as a jet of gas burning at the end of a

mouth blowpipe, is passed across the surface of the oil once for every 2° F. rise in temperature, care being taken that the flame does not come in actual contact with the oil.

The temperature at which a flicker of flame covers the whole surface of the oil is taken as the *open flash* temperature. The heating is continued, and the test flame applied periodically as before. When the oil continues to burn until the next application of the test flame is due, the temperature recorded is taken as the *fire test*.

If a given mixture contains ONLY A SMALL PERCENTAGE of light oil, it will be found, on repeating the "closed," "open," and "fire" tests with the same sample, that the second "closed" test flash point will be considerably higher than the first. Less difference will be found between the two "open" tests, whilst the temperature registered for the "fire" tests will be practically in agreement.

This is due to the fact that, during the first series of tests most of the light oil is removed. These tests thus give some idea as to the homogeneous character of the given mixture.

To illustrate this, a small quantity of light petroleum may be added to a sample of lubricating oil, and the "closed," "open," and "fire" tests carried out. The tests should then be repeated, using the same sample.

DETECTION OF PETROLEUM VAPOUR.

On account of the explosive nature of petrol vapour, it is often of great importance to detect the presence of this substance in air, and to estimate its amount. This is effected by what is known as the Clowes-Redwood Method, which depends on the formation of a "cap" over the flame of a safety lamp, as in the detection of fire damp in the air of mines.

The apparatus* employed, shown in the diagram Fig. 30, consists of a safety lamp A, in which hydrogen from the cylinder B is burned. The sample of air to be tested is contained under pressure in the cylinder C. The lamp is so constructed that the flame cannot travel to the mixture in this cylinder. The cloth shown at the back is to darken the lamp during an observation.

The working of the test is described as follows by Sir Boverton Redwood. ("Proceedings of the Institute of Civil Engineers," 1893-4, 116, Part II.)

* The following description is adapted, by permission, from Clowes and Redwood's "Detection of Inflammable Vapour" (Crosby Lockwood and Son) and J. A. Hicks' "Mineral Oil Testing" (C. Griffin).

"In the use of the apparatus the first step is to connect the hydrogen cylinder with the lamp, taking care that the unions are screwed up gas-tight. The sliding chimney of the lamp being raised about halfway, the gas is then cautiously turned

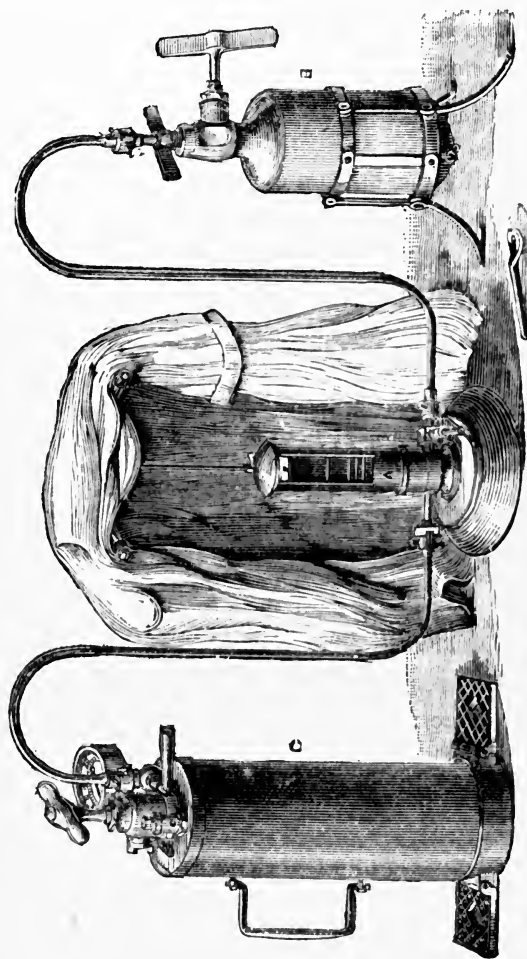


FIG. 30.—Apparatus for the detection of petroleum vapour.

on at the cylinder, the regulating valve on the lamp being left open, and a light is applied to the hydrogen jet. The valve on the hydrogen cylinder is then adjusted so as to give a flame rather more than 10 millimetres (0·4 inch) in length and the lamp chimney pushed down until there is an opening

of only about a quarter of an inch in height at the bottom. This opening is left for the supply of air to the hydrogen flame during the few minutes occupied in the warming of the chimney. As soon as the moisture which at first condensed upon the cold glass has evaporated the lamp is ready for use, and assuming the collecting vessel to have been already charged with the sample to be tested, and connected with the lamp, all that remains is for the observer to close completely the sliding chimney of the lamp, adjust the hydrogen flame by means of the regulating valve on the lamp, so that the tip of the flame is only just hidden when the eye of the observer is on a level with the bottom of the window, place his head under a cloth such as is used by the photographers so as to exclude light, and as soon as his eyes have become sufficiently sensitive, turn on the tap of the collecting cylinder, and carefully observe what takes place in the lamp chimney.

"The tap may at once be turned on fully, as the construction of the outlet and inlet orifices prevents the sudden rushing out of the contents of the cylinder, and the sample will be gradually delivered into the test lamp during a period of more than two minutes, which is ample time for noting the effect. The rate of delivery is, of course, a gradually diminishing one, but this is not found to be attended with any inconvenience, the conditions being the same in each experiment.

"In this way a proportion of vapour, considerably below that which is required even for the production of an inflammable mixture, and still lower than that which is needed to give an explosive atmosphere, may be detected by the formation of a flame cap of greyish-blue colour, which, though faint is easily seen, especially after a little practice.

"With an increase in the quantity of vapour, the flame-cap first becomes much better defined, though it is not greatly augmented in size, and then considerable enlargement of the cap occurs, this condition being arrived at before the atmosphere becomes inflammable.

"In taking a sample of the air in a tank the collecting vessel may be used in the tank if the proportion of vapour present is known to be small; but even in such cases it is better to employ a short suction tube, the open end of which can be placed at the lower point in the tank, where most vapour would probably be found. If, on the other hand, the atmosphere of the tank is suspected to contain so much vapour that there would be danger of its producing insensibility when taken into the lungs, and especially if the compartment is

entered through a small manhole, it would obviously be most improper that any one should be sent into the tank, and in that case the sample should be taken by the use of a long suction tube reaching to the bottom."

A portable form of the above apparatus is described in Clowes and Redwood's "Detection of Inflammable Gas and Vapour," p. 181 (Crosby Lockwood and Son).

In this apparatus a small hydrogen cylinder is attached

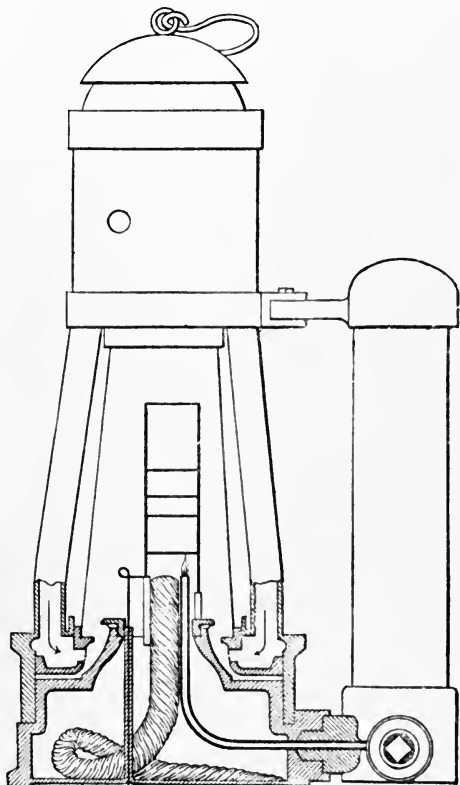


FIG. 31.—Hydrogen lamp.*

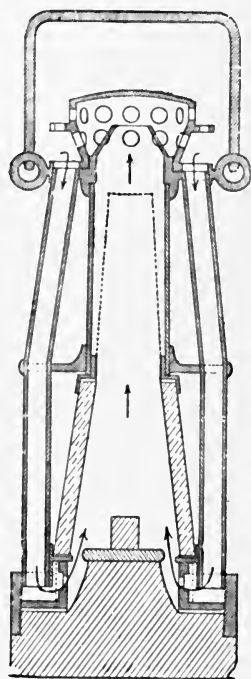


FIG. 32.—Gray oil lamp.*

directly to the lamp, and the air to be tested, drawn from some receptacle by means of a rubber tube, is forced into the lamp by means of a ball syringe arrangement.

* Taken from Messrs. Clowes and Redwood's "Detection of Inflammable Gas and Vapour" (Crosby Lockwood and Son), by permission of the publishers.

The amount of petroleum vapour (or gas) is determined from the height of the cap when this has become constant.

For the detection of petroleum vapour an ordinary hydrogen safety lamp, as shown in the diagram Fig. 31, may be employed.

This is a modification of the Gray oil lamp shown in section in Fig. 32, in which the direction of the gas is shown by the arrows and the gauze indicated by dotted lines.

When the hydrogen jet is lighted, the oil flame can be extinguished by drawing down the wick by means of a wire passing through the base of the lamp.

A few drops of petrol should be placed in a large glass vessel in a dark room, and on the introduction of the lamp into the vessel the characteristic cap will be observed.

Only in places where no "cap" at all is shown with this apparatus should a naked light be employed.

For further details as to the height of "cap" obtained in air containing known amounts of pentane vapour, etc., see Thomson, Redwood and Cooper-Key's "Handbook on Petroleum" (Griffin), p. 117; Clowes and Redwood's "Detection of Inflammable Vapour" (Crosby Lockwood and Son).

Another method for the detection of petroleum vapour has been devised by Philip and Steele (English Patent No. 22,129 of 1906). This depends on the rise in temperature experienced by a platinum or palladium wire when surrounded by a mixture of inflammable gas and air. This is an example of catalytic oxidation.

2u 0

HCO

HO

CO₂

CHAPTER IX

DETECTION AND ESTIMATION OF ELEMENTS, ETC.

DETECTION OF CARBON AND HYDROGEN

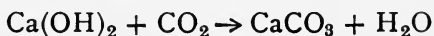
WHEN an organic compound is heated strongly with copper oxide, the hydrogen of the substance combines with oxygen to produce water, and the carbon gives rise to carbon dioxide. The copper oxide is reduced to metallic copper.

Dry some copper oxide by heating it in a porcelain basin for about ten minutes, and allow it to cool in a desiccator. Fill a hard glass test-tube to a depth of about one inch with some of the dry copper oxide. Mix about a quarter of a gram of dry powdered sugar with about ten times its weight of the dry oxide, and introduce the mixture into the tube. Add more dried oxide until the tube is about three-quarters full. Insert a cork carrying a delivery tube, the end of which should dip under lime water.

Tap the tube gently to ensure a free passage for the gas over the copper oxide. Heat strongly, commencing at the end nearer the cork. (*Move the burner to and fro quickly, at the commencement, or the test-tube will break.*)

When the front part of the tube is hot, that portion containing the mixture may be heated.

The water which is formed in the experiment condenses in the delivery tube, and the presence of the carbon dioxide is detected by its action on the lime water.



DETECTION OF NITROGEN.

Soda-lime Method.—Many nitrogenous substances (but not all) when heated with soda lime give off ammonia gas.

Heat a small quantity of urea with about five times its weight of soda lime.

Detect the ammonia by—

- (1) Its smell,
- (2) Its action on moist red litmus paper.
- (3) The formation of white fumes when a rod dipped in strong hydrochloric acid is brought to the mouth of the tube.

Sodium Method.—Most nitrogenous organic substances, when heated with metallic sodium, give rise to sodium cyanide (NaCN).

In a DRY test-tube place a small piece of sodium, about the size of a pea, and heat it till it melts.

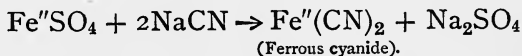
Add gradually a small quantity of acetanilide, heating after each addition. A violent reaction takes place at first, but after a short time the tube may be heated strongly. Continue heating for some minutes until all action has ceased, and place the tube while still hot in a small porcelain dish containing about 5 c.c. of water. This will, of course, break the tube, and the liquid should now be boiled and filtered. The filtrate is *alkaline*, owing to the presence of sodium hydroxide. It is tested for the presence of a cyanide in the following manner.

To the solution add a small quantity of solid ferrous sulphate and boil; sodium ferrocyanide is produced and remains in solution, ferrous hydroxide being precipitated. A few drops of ferric chloride solution are then added, some of which is probably converted into ferric hydroxide.

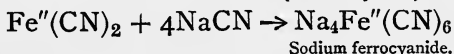
On making the solution strongly acid with hydrochloric acid, a *blue solution* or a *precipitate* of Prussian blue is obtained, and the ferrous hydroxide, along with any ferric hydroxide which is present, is dissolved.

The production of this substance denotes the presence of nitrogen in the original compound.

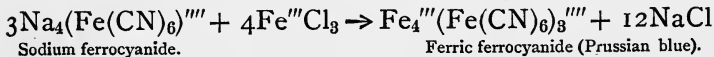
[It should be noted that the presence of free hydrochloric acid is necessary, since the Prussian blue is decomposed by alkalis.]



(Ferrous cyanide).



Sodium ferrocyanide.



Sodium ferrocyanide.

Ferric ferrocyanide (Prussian blue).

DETECTION OF HALOGENS.

1. Heat a piece of copper wire in the Bunsen burner until the green colour which is at first imparted to the flame

entirely disappears. Allow to cool, and then place on the copper wire a portion of the substance to be tested for halogen (such as chloroform). Heat in the Bunsen flame. A green coloration is produced, due to the presence of a copper halogen compound.

2. Heat a small quantity of an organic substance containing halogen (such as *p*-chloronitrobenzene) with excess of lime (free from halogen). When cool, shake out the contents of the tube into a beaker containing distilled water, acidify with nitric acid and boil. Add silver nitrate, and the silver halogen compound will be precipitated.

DETECTION OF SULPHUR.

1. Many organic sulphur compounds, on fusion with potassium nitrate and sodium carbonate produce alkali sulphate. Mix about $\frac{1}{4}$ gram of thiourea with about six times its weight of a mixture of potassium nitrate and fusion mixture. Heat over the Bunsen flame on platinum foil until a clear liquid is obtained. Allow to cool, dissolve in water, acidify with nitric acid, and test for sulphate by the addition of barium chloride.

2. Proceed as in the test for nitrogen (sodium method). Instead of adding iron salts test the solution for sulphide by

(a) action on silver coin which gives a black stain on acidifying ;

(b) addition of a solution of sodium nitroprusside, which produces a deep violet coloration.

Certain classes of easily decomposed sulphur compounds occasionally present in oils give sodium sulphide when the oil is boiled with metallic sodium ; any sulphuric acid left in the oil after refining would give rise to sulphate and not sulphide.

Some of the oil may be boiled with some pieces of metallic sodium for twenty minutes in a flask fitted with a reflux condenser. When quite cold, water is added very gradually to remove the excess of sodium. The presence of sodium sulphide is detected by the addition of sodium nitroprusside as before.

In addition to the sodium method described above, the following test is often employed for the detection of sulphur in an oil :—

A small quantity of the oil is boiled with an equal volume of alcohol and a few drops of ammonium hydroxide solution. On the addition of silver nitrate solution, a brown coloration

indicates the presence of a sulphur compound in the oil. (See Redwood, "Treatise on Petroleum," vol. ii. page 318.)

DETECTION OF SULPHURETTED HYDROGEN AND SULPHURIC ACID IN OILS.

It occasionally happens that a crude oil contains free sulphuretted hydrogen. The presence of this substance may be detected by shaking some of the oil with distilled water and adding a few drops of an alkaline solution of sodium nitroprusside, when a violet coloration will be produced if sulphuretted hydrogen is present.

Sulphuric acid is occasionally found in oils which have been purified by means of this substance (see page 68) owing to insufficient treatment with alkali or incomplete washing; its presence may be detected by shaking the oil with distilled water and subsequent addition of a solution of barium chloride, when a turbidity due to the formation of barium sulphate will be produced.

THE QUANTITATIVE ESTIMATION OF ELEMENTS IN ORGANIC SUBSTANCES.

It is not proposed to describe in detail the various processes adopted in such determinations, except in the case of the element sulphur, the quantitative estimation of which is often of extreme importance in connexion with the various uses of petroleum and its substitutes. For methods of determining the empirical and molecular formulæ of compounds from the results of analysis, other text-books should be consulted.

The Estimation of Carbon and Hydrogen.—The principles underlying this estimation are the same as those made use of in the qualitative detection of these elements. A weighed quantity of the substance is burned in a tube containing copper oxide and through which a stream of air or oxygen is passed. The amounts of water and carbon dioxide produced are weighed, the former being absorbed by means of sulphuric acid and the latter by potassium hydroxide solution. Various modifications of the process are necessary if the substance contain, for example nitrogen, halogens, sulphur, etc.

Although the principles underlying these operations are so simple, the actual determination is one which requires great skill to ensure accuracy.

An account of this "combustion" process will be found in Cohen's "Practical Organic Chemistry" (Macmillan and Co.).

Special attention should be paid to the modification of the process necessary for the combustion of a volatile liquid.

The Estimation of Nitrogen.—Various methods are employed according to the nature of the substance under examination and the accuracy to which the results are required.

The method which is most accurate and is applicable to all nitrogenous organic substances is that known as the Dumas method. In this process a weighed quantity of the substance is heated in a hard glass tube with copper oxide. The carbon and hydrogen are converted into carbon dioxide and water respectively and the nitrogen set free, which can then be collected over a solution of potassium hydroxide and its volume measured. Before the substance is heated the air in the tube is completely removed either by means of a stream of carbon dioxide or by exhaustion with a Sprengel pump.

For practical details see Cohen's "Practical Organic Chemistry."

Another process for the estimation of nitrogen in a substance which is often employed in technical analysis, is that known as the Kjeldahl method. It is not applicable to all nitrogenous organic compounds, but it can be employed in many cases.

In this method a weighed quantity of the substance is heated with concentrated sulphuric acid containing potassium sulphate which serves to raise the boiling point of the mixture and prevent the vaporizing of the acid. By this treatment the nitrogen in the substance is converted wholly into ammonium sulphate. The mixture on distillation with excess of sodium hydroxide gives ammonia which is passed into a measured volume of a standard solution of an acid. From the amount of acid neutralized the amount of ammonia which has been absorbed is found. From this the weight of nitrogen in the given weight of substance, and hence its percentage of nitrogen may be obtained.

For practical details see Clowes and Coleman, "Quantitative Analysis" (J. and A. Churchill), 9th edition, p. 417.

The Estimation of Halogens.—The method of Carius is the one usually employed. A weighed quantity of the substance is heated with not more than 15 drops of fuming nitric acid

and excess of solid silver nitrate in a sealed tube. The halogen is thereby converted into an insoluble silver halogen salt, which can be weighed. Taking the composition of this salt as known, the weight of halogen contained in a given weight of it may be calculated, and hence the percentage of halogen in the original substance found.

These determinations, and the following one under sulphur, in which use is made of sealed tubes, should be carried out a first time under strict supervision, otherwise a serious accident may occur.

For the practical details of the Carius method, see Cohen's "Practical Organic Chemistry."

The Estimation of Sulphur.—The determination of the amount of sulphur in an organic substance, solid or liquid, may be carried out by the Carius method, which is essentially the same as that employed in the estimation of halogens.

The substance is heated in a sealed tube with not more than 15 drops of fuming nitric acid, and the sulphur is thereby converted into sulphuric acid, the amount of which is estimated by conversion into insoluble barium sulphate, which is weighed. Taking the percentage of sulphur in barium sulphate as known, the weight of sulphur in a given weight of the original substance, and hence its percentage of sulphur is found.

Since 1 gram molecule of barium sulphate (233 grams) contains 1 gram atom of sulphur (32 grams) $\frac{32}{233} = 0.1373$ of any weight of barium sulphate is sulphur.

For practical details, see Cohen's "Practical Organic Chemistry."

The amount of sulphur in a combustible gas or a liquid such as paraffin oil, is conveniently determined by burning a measured volume of the gas or known weight of the liquid, whereby the sulphur is converted to sulphur dioxide, which by means of an oxidizing agent is converted into sulphuric acid. The amount of this substance which is produced is determined by precipitation as barium sulphate.

Another method which is now largely employed and is capable of universal application is that of the complete combustion of a weighed quantity of an oil in excess of oxygen under pressure in the bomb used in calorimetric determinations (see page 310). The sulphuric acid, formed

both directly and by the oxidation of any sulphur dioxide produced in the combustion, is estimated as before by conversion into barium sulphate.

Many other determinations such as that of sulphur in coal depend on the same principle of conversion into sulphuric acid or soluble sulphate and subsequent precipitation and weighing of the barium sulphate so produced.

It is thus obvious that the estimation of sulphuric acid or a sulphate in solution is extremely important in connexion with the determination of the sulphur content of a substance. In the case of sulphates it is more usual to express the result as percentage of sulphate radical than as sulphur.

For practice in this estimation the determination of the percentage of "sulphate radical" (SO_4) in a soluble sulphate such as potash alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ should be undertaken.

Estimation of Sulphur in a Soluble Sulphate.—Two separate determinations should be carried out simultaneously.

From 0.2 to 0.4 gram of the alum is weighed out accurately from a weighing bottle and transferred to a lipped beaker of about 300 c.c. capacity covered with a clock glass. About 75 c.c. of distilled water and about 10 c.c. of dilute hydrochloric acid are added and the solution heated to boiling.

About 20 c.c. of an approximately 20 per cent. ammonium chloride solution are then added and the solution kept *gently* boiling whilst a boiling solution of barium chloride is added until no further precipitate is produced on adding more of this reagent.

(The object of adding the ammonium chloride and precipitating in boiling solution is to ensure that the barium sulphate shall be granular and will rapidly subside and be easily filtered.)

The mixture is allowed to stand until the precipitate has subsided, the clear liquid is then poured off through a special filter paper, using a glass rod to prevent liquid from running down the outside of the beaker and taking care not to disturb the precipitate. The precipitate is then washed three times by decantation with hot water, the washing water being poured through the filter. Finally, the precipitate is transferred to the filter by means of a jet of hot water from the wash bottle. It is then washed with hot water until the filtrate is free from chloride, as shown by testing with silver nitrate. During the last washings the precipitate should be collected as far as possible into the apex of the funnel. (At no point should

the precipitate have been allowed to come within less than 1 cm. of the top of the filter paper.)

The funnel is then covered securely with a perforated wet filter paper and placed in a steam oven to dry.

The *dry* precipitate is next detached *as completely as possible* from the filter paper and transferred to a clean, dry, previously weighed porcelain or platinum crucible, provided with a lid, this operation and the next being carried out over a sheet of black glazed paper. The filter paper is then rolled up with the remaining precipitate on the inside and burnt in a coil of platinum wire.

The white ash is deposited on a clear space on the bottom of the crucible, which has previously been tapped to remove the precipitate to one side. Any precipitate or ash which has fallen on to the glazed paper is then transferred to the crucible by means of a camel's hair brush.

The barium sulphate which is left adhering to the filter paper will, on the combustion of the latter, be converted to barium sulphide. This must be reconverted to sulphate before weighing. One drop of dilute hydrochloric acid is allowed to fall on the ash, followed by one drop of dilute sulphuric acid.

The crucible is partially covered with its lid, which is inverted, and heated *very gently* to remove the acids. Finally, when no more vapour escapes it is heated to a red heat for about fifteen minutes. It is then allowed to cool in a desiccator and weighed. It is again heated, cooled, and weighed and the process repeated until the weight is constant.

From the increase in weight of the crucible the weight of barium sulphate is found after deducting the weight of the ash of the filter paper.

This weight of barium sulphate $\times 0.4115$ gives the weight of (SO_4) radical in the weight of alum originally taken, and from this the percentage of (SO_4) radical in the substance is calculated.

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ requires $SO_4 = 40.5$ per cent.

ESTIMATION OF SULPHUR IN COAL AND COKE.

The coal is heated with a mixture of sodium carbonate and magnesium or calcium oxide whereby the whole of the sulphur is converted into soluble sulphates. From the amount of barium sulphate produced on precipitation the percentage of sulphur in the coal can be found.

Weigh out accurately about 1.5 grams of the *finely powdered* coal into a platinum crucible and mix it thoroughly by means of a glass rod with about twice its weight of a mixture of pure dry sodium carbonate and magnesium oxide or lime (free from sulphate) in the proportions 1 : 2.

Partially cover the crucible with its lid and heat very gently so as not to produce any smoke from the coal. Gradually raise the temperature nearly to redness and continue the heating until no black specks of carbon remain. The mass should now be almost white if the combustion is complete, or slightly red if iron oxide is present.

When it is cool treat the mass with water (about 75 c.c.) in a beaker, warm and filter. Rinse out the crucible and beaker and pour the washings through the filter. Add about 15 c.c. of a saturated aqueous solution of bromine to oxidize any sulphite to sulphate ($\text{Br}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HBr}$). The liquid is then acidified with dilute hydrochloric acid to decompose the carbonate present and boiled until the bromine is removed.

The sulphate is next precipitated by the addition of a hot solution of barium chloride to the boiling liquid, ammonium chloride solution having previously been added (see page 165). The precipitate is treated as described before.

The weight of the barium sulphate obtained $\times 0.1373$ gives the weight of sulphur in the amount of coal used for the experiment.

It should be noted that in this estimation the crucible should be heated by means of a spirit lamp on account of the sulphur dioxide which is present in the products of combustion of coal gas.

The determination of the amount of sulphur in coal may also be carried out by means of the bomb used in calorimetric determinations, as described on page 172 in connexion with the estimation of sulphur in petroleum. One gram of the coal is placed in the crucible of the bomb, a small quantity of water being placed at the bottom of the bomb. Oxygen is then passed in up to a pressure of 25 atmospheres. The products of combustion are treated as described on page 172.

ESTIMATION OF THE ASH IN COAL AND OF SULPHUR IN THE ASH.

(a) **Estimation of the Ash.**—Weigh out accurately about 2 grams of finely powdered coal into a weighed porcelain

boat. Place the boat on some teased asbestos in a combustion tube and heat the tube gradually to redness in a combustion furnace. A slow stream of air is drawn through the tube by means of an aspirator or water pump, and the heating continued until all the dark coloured combustible matter has disappeared. The boat is allowed to cool and when cold is reweighed; from the loss in weight the percentage of ash in the coal is obtained. (The teased asbestos serves to prevent the boat from sticking to the tube if the latter is allowed to soften through overheating.)

The ash in coal may also be estimated by heating a weighed quantity of the coal in a porcelain crucible until all the combustible matter has disappeared, and noting the loss in weight of the crucible and contents.

(*b*) **Estimation of Sulphur in the Ash.**—The contents of the porcelain boat (obtained in the previous estimation) are transferred completely to a beaker, treated with a little water containing dilute hydrochloric acid, heated nearly to boiling, filtered and the residue washed. The solution contains sulphates in which form all the sulphur contained in the ash is present. The sulphate is determined as before by means of barium chloride, and from the weight of barium sulphate obtained the amount of sulphur present in the ash may be calculated.

Sulphur in the Volatile Matter of Coal.—The total sulphur in the *volatile* matter of coal is equal to the total sulphur in the coal *minus* the total sulphur in the coke.

Sulphur in Coke.—This is made up of two portions, (*a*) the sulphur which is left as sulphate in the ash, and (*b*) the sulphur in the combustible portion of the coke.

The total sulphur in coke could be determined in a manner similar to that of the estimation of the total sulphur in coal. It is, however, often of importance to determine the sulphur in the combustible portion of the coke, known as the volatile sulphur of the coke.

This last estimation, although not dependent on the formation of barium sulphate, is mentioned here in order to complete the determinations of sulphur in coal and coke. It is accomplished by burning the coke in a current of oxygen, whereby the sulphur is converted to sulphur dioxide. The products of combustion are passed through a measured volume of a

standard solution of iodine in potassium iodide when the following reaction takes place:—



The amount of iodine remaining in solution is determined by titration with a standard solution of sodium thiosulphate (see page 177) and from the amount of iodine required for the sulphur dioxide, the amount of the latter and hence the weight of sulphur contained in the coke is found.

ESTIMATION OF SULPHUR IN COAL GAS.

Referees' Method.—A measured volume of gas at known temperature and pressure is burnt in air which contains ammonia gas, all the sulphur compounds in the gas under these conditions are oxidized to sulphur dioxide or sulphuric acid, which combine with the ammonia. The water, ammonium carbonate, sulphite, and sulphate produced, are collected in a condensing tower. After the combustion, the sulphite is converted into sulphate by means of bromine water and the total sulphate precipitated by the addition of barium chloride.

In this determination the apparatus employed is shown in the diagram Fig. 33. The coal gas is measured by passing through a meter previously freed from air by the passage of some of the gas. This preliminary passage of the gas also serves to saturate the water in the meter with the gas under examination. A manometer is attached to the meter to denote the excess of pressure of the gas over that of the atmosphere. The temperature and pressure of the gas passing through the meter are noted periodically during the entire process.

The gas passes from the meter to a small Bunsen burner supported on a perforated metal base. Freshly broken lumps of ammonium carbonate (about 40 grams) are placed round the foot of the burner, and from the slow decomposition of this substance ammonia is produced, which combines with water and sulphur dioxide produced during the combustion and so prevents the escape of the latter.

The products of combustion pass up the conical chimney into a condensing tower filled with glass balls about 1.5 cm. diameter. A glass tube is fixed into the bottom of this tower and by this means the condensed products of combustion may be drawn off periodically into a beaker placed below.

A few pieces of ammonium carbonate are placed on the

top of the glass balls in the condensing tower. A wide glass tube is attached in a sloping position to the top of this tower to act as a reflux condenser.

The height of the flame is adjusted by means of a screw clip on the tube of the Bunsen burner, so that the gas passes through the meter at not more than 20 litres per hour. If the gas is burnt at a greater rate than this some of the sulphur dioxide will probably escape absorption.

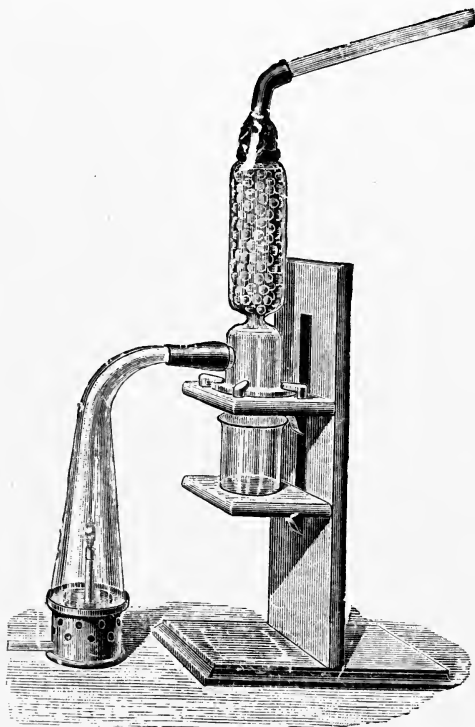


FIG. 33.—Apparatus for the estimation of sulphur in coal gas.

When from 50 to 60 litres of the gas have been burned, the supply tap is turned off, after taking a final reading of the temperature and pressure of the gas passing through the meter.

The mean temperature and pressure readings are taken as the temperature and pressure of the gas used in the experiment.

The condensing tower is rinsed out by pouring four portions of distilled water each of about 25 c.c. through the

sloping tube. The conical chimney is also rinsed out and the washings added to the contents of the beaker.

About 3 c.c. of a saturated aqueous solution of bromine, free from sulphate, is then added and the liquid thoroughly stirred and allowed to stand a few minutes. The solution is then acidified gradually with dilute hydrochloric acid and boiled to expel carbon dioxide and bromine.

The sulphate is then precipitated by means of a boiling solution of barium chloride, the precipitate treated as described before and finally weighed.

From the weight of barium sulphate obtained, the weight of sulphur in the volume of gas burned is found. The volume of the gas is reduced to 0° C. and 760 mm. pressure, and the result expressed as grams of sulphur per cubic metre (1000 litres) of the gas at N.T.P.

In reducing the volume of the gas burned to N.T.P. it should be noted that the pressure due to the coal gas in the meter is equal to atmospheric pressure at the time of the experiment *plus* the pressure indicated by the manometer *minus* the pressure of aqueous vapour at the temperature of the water in the meter.

By means of the relations, 1 cubic foot = 28.32 litres and 1 grain = 0.0648 gram, the sulphur content of the gas may also be expressed as "grains of sulphur per 100 cubic feet."

The sulphur content of illuminating gas does not usually exceed 22 grains of sulphur per 100 cubic feet, and the gas should be entirely free from sulphuretted hydrogen.

ESTIMATION OF SULPHUR IN OILS.

The bomb method described under light oils (*c*), is applicable to any oil; other methods, however, are used in special cases.

(a) **Burning Oils, Kerosenes.**—The estimation of the percentage of sulphur in a lamp oil may be carried out in a manner similar to the above determination of sulphur in coal gas. The oil is burned from a small lamp, which is weighed before and after the experiment.

In some cases the oil is mixed with absolute alcohol and the mixture then burned, care being taken that the flame is non-luminous. Several fresh quantities of absolute alcohol are added to ensure that the whole of the oil is burned. A similar method is applicable to light oils.

Good burning oils do not as a rule contain more than 0.02 per cent. of sulphur. An excess of sulphur is obviously

objectionable on account of the unpleasant nature of sulphur dioxide.

(b) **Heavy Oils.**—This determination is carried out by employing a modification of the process adopted for the estimation of sulphur in coal.

From 0.75 to 1.5 grams of the oil are weighed into a very small platinum crucible which contains about 4 grams of a mixture of pure dry lime and sodium carbonate in the proportions of four parts of the former to one of the latter. The contents of the crucible are then thoroughly mixed by means of a thin glass rod and the crucible filled with more of the mixture, during which process any oil adhering to the glass rod is completely removed.

A large platinum crucible is inverted over the smaller one so that the top of the latter is in close contact with the bottom of the former. The whole is then inverted and more of the mixture of lime and sodium carbonate placed in the larger crucible until the smaller one is just covered.

A piece of thick asbestos millboard is placed over the larger crucible and the whole transferred to a previously heated muffle furnace. Owing to the presence of the asbestos, the oil does not become hot until the mixture of lime and sodium carbonate is already heated. After five minutes the asbestos is removed and the heating continued for two hours. The mixture is then treated as described under the estimation of sulphur in coal.

(c) **Light Oils.**—The most reliable method is that in which the substance is burned in excess of oxygen under pressure in a bomb, as used in calorimetric determinations (see page 310).

From 1 to 2 grams of the light oil are weighed into the platinum capsule of the bomb, the coil of iron wire adjusted so as to come practically into contact with the oil and oxygen admitted up to 30 atmospheres pressure. The liquid is then fired, and after a short time the gas is slowly allowed to bubble through a dilute solution of sodium hydroxide (free from sulphate) to free it from any sulphur dioxide or sulphuric acid which it might carry over. The sodium hydroxide is neutralized with hydrochloric acid and a few drops of bromine water are added.

The bomb is then opened and washed out three times with small quantities of distilled water, the washings are added to the solution obtained above, and the mixture heated to boiling, to expel the bromine. The liquid is filtered, if necessary, and the sulphate precipitated in boiling solution by means of a boiling solution of barium chloride.

ESTIMATION OF WATER IN OILS.

If the oil is not appreciably volatile below 110° C. the water may be estimated by heating 25 grams of the sample in a weighed porcelain basin to this temperature on a sand bath, stirring constantly with a thermometer until no more steam is formed (see Bumping, page 98). The basin is allowed to cool and is weighed. From the loss in weight the percentage of water in the sample is calculated.

The water in volatile oils may be determined by means of an apparatus known as a Sutherland bulb.* Fig. 34.

The principle of this method is that water separates more readily from an oil when the latter is heated.

A weighed quantity of the sample is introduced into the apparatus, and the stopper securely tied down by means of string. A piece of rubber tissue is tied over the stopper to prevent the entrance of condensed steam. The apparatus is then kept in a bath of water at about 80° C. until the volume of the water which separates out is constant.

If the water does not readily separate out, owing to the viscosity of the oil, the sample may be diluted with a known amount of kerosene which is free from water or of which the water content is known.

From the volume of water obtained at, say, 80° C. its weight may be determined and hence the percentage by weight of water in the oil found.



FIG. 34.—Sutherland bulb.

The percentage of water in a substance such as coal tar may be determined by the careful distillation of about 250 grams of the substance; (see page 98, *re* Bumping), the distillation being continued until no more water comes over. The water in the distillate, which consists of light oils and water (lower layer), may be measured by transferring the distillate to a measuring cylinder, and hence the percentage of water in the original substance found.

In the case of viscous oils, some dry xylene is often added before distillation, and the mixture distilled until no more water passes over.

* See also J. A. Hicks' "Mineral Oil Testing" (C. Griffin).

Acetylene Method.—The amount of water in oils can also be estimated by measuring the volume of acetylene liberated by the action of a known amount of the moist oil on calcium carbide, the gas being measured by a displacement of a salt solution. For details of the method, see a paper by Roberts and Fraser, *Four. Soc. Chem. Ind.*, 1910, p. 197.

CHAPTER X

THE DETECTION AND ESTIMATION OF UNSATURATED HYDROCARBONS IN LIQUID MIXTURES

DETECTION.

IT has been pointed out under ethylene and acetylene, pages 10-15, that these substances, as well as unsaturated compounds in general, have the power of combining directly with bromine and other halogens, and with concentrated sulphuric acid; also, that unlike the corresponding saturated compounds, they are readily acted upon by oxidizing agents, such as potassium permanganate. These reactions may be made use of in the detection and estimation of olefine and acetylene hydrocarbons in liquid mixtures.

Bromine Test.—To a sample of an oil such as a light shale oil, or a petrol, a solution of bromine in carbon disulphide is added drop by drop. The immediate decolorization of the bromine denotes the presence of an unsaturated compound, probably an olefine.

After a time the decolorization takes place more slowly, and acid fumes may be given off from the mixture. If this is the case bromine is being *substituted* for hydrogen in one or more of the compounds present, the hydrogen so displaced combining with bromine with the formation of hydrogen bromide.

This is especially the case if the reaction is carried out in direct sunlight.

Potassium Permanganate Test.—To another portion of the sample a few drops of a dilute solution of potassium permanganate are added and the mixture vigorously shaken. If olefine hydrocarbons are present the colour of the permanganate will be changed to brown.

Sulphuric Acid Test.—50 c.c. of concentrated commercial sulphuric acid are placed in a dry, 100 c.c. measuring cylinder, fitted with a glass stopper. Some of the light oil to be tested, previously dried by shaking with anhydrous calcium chloride,

is added gradually until the total volume is 75 c.c. The mixture is vigorously shaken at intervals for a quarter of an hour and then allowed to stand until the oil has completely separated from the acid. From the diminution in volume of this upper layer the amount of the unsaturated hydrocarbons in the light oil is found. This method, however, for various reasons is only approximate.

ESTIMATION.

The determination of the amount of unsaturated hydrocarbon in a liquid mixture is a matter of considerable importance.

In addition to the sulphuric acid method just described, for the comparison of the olefine content of two samples of oil, equal quantities of the two substances may be treated with equal volumes of a bromine solution or a solution of potassium permanganate of known strength. By determining the excess of the reagent remaining in solution after treatment with the oil, the amount of bromine or potassium permanganate removed from solution can be found, and from this a comparison made of the amount of unsaturated hydrocarbons present in the given samples.

The bromine method is the one most usually adopted, the result being expressed as grams of bromine absorbed by one hundred grams of the oil. The actual percentage of unsaturated hydrocarbons in such a mixture cannot be determined accurately, since, if acetylene hydrocarbons are present, one molecule of such a substance might absorb either two or four atoms of bromine as follows:—



or



Also a certain amount of bromine is used in substitution and not direct addition; this is especially the case if the oil under examination contains aromatic hydrocarbons.*

The determination of the amount of bromine absorbed is carried out as follows:—

25 c.c. of a solution of the oil in dry carbon disulphide, containing 2–4 grams of the substance per 100 c.c., is placed in a dry glass stoppered bottle and treated with 25 c.c. of a

* For the methods employed in the examination of an oil which contains paraffin, olefine, naphthene, and benzene hydrocarbons, see page 212.

solution of bromine in carbon disulphide, which is approximately decinormal. The mixture is kept in a dark place for 15 minutes (see page 179), excess of potassium iodide solution is then added and the iodine liberated removed by the addition of decinormal sodium thiosulphate solution, using starch as indicator.

From the difference between the volumes of thiosulphate solution required for 25 c.c. of the bromine solution in a blank experiment and in the actual test, the amount of decinormal sodium thiosulphate equivalent to the bromine absorbed is found.

Equations—



and



One litre of a normal solution of sodium thiosulphate is equivalent to 1 litre of a normal solution of iodine, and hence to 1 litre of a normal solution of bromine, which contains 80 grams of bromine per litre.

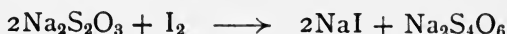
\therefore 1 c.c. N/10 sodium thiosulphate solution = 0.008 grams of bromine.

By making use of this result the weight of bromine absorbed by a given weight of the oil may be found, and hence the amount absorbed by 100 grams calculated.

The solutions required for the estimation are prepared as follows:—

Decinormal sodium thiosulphate solution.

From the equation



1 gram molecule iodine (2×127 grams) is equivalent to 2 gram molecules of sodium thiosulphate. Crystallized sodium thiosulphate contains 5 molecules of water of crystallization; that is 127 grams of iodine are equivalent to—

$$\text{Na}_2 \quad \text{S}_2 \quad \text{O}_3 \quad 5\text{H}_2\text{O} \\ 46 + 64 + 48 + 90 = 248 \text{ grams of the crystallized salt.}$$

$$\begin{aligned} 1 \text{ litre of decinormal iodine solution} &= 12.7 \text{ grams iodine} \\ &= 24.8 \text{ grams crystal-} \\ &\quad \text{lized sodium thiosulphate.} \end{aligned}$$

Hence, 1 litre of decinormal sodium thiosulphate contains 24.8 grams of the crystallized salt, or 1 c.c. decinormal sodium thiosulphate solution = 0.0127 gram iodine.

25 grams of the pure crystallized salt, previously dried by

pressing between sheets of filter paper are weighed out, dissolved in water and the solution diluted to 1 litre.

For the present purpose and for use in connexion with the iodine value of oils, page 288, this solution may be regarded as strictly decinormal. If greater accuracy is required its exact strength may be determined by means of a standard solution of iodine, or indirectly by standard potassium dichromate or permanganate solutions as described in text-books of Practical Inorganic Chemistry.

Starch Solution.—About 1 gram of powdered starch is rubbed to a thin paste with a little water, and then poured into about 100 c.c. of boiling water.

Decinormal Solution of Bromine in Carbon Disulphide.—N/10 bromine solution contains 8 grams of the substance per litre.

(The density of bromine = 3.18, or 1 c.c. bromine = 3.18 grams.)

Measure out 380 c.c. of freshly distilled carbon disulphide and add 1 c.c. of bromine * from a burette. The solution will be approximately decinormal.

Some anhydrous calcium chloride should be added to the bromine solution which should then be stored in a dark cupboard.

Suppose in a particular estimation—

weight of stoppered weighing bottle empty = 12.463 grams

“ “ “ “ + oil = 16.383 “

weight of oil = 3.92 “

Some dry carbon disulphide was added and the contents of the weighing bottle transferred by means of a funnel to a 100 c.c. measuring flask. The weighing bottle was rinsed out several times with small quantities of carbon disulphide, which were transferred to the graduated flask. Finally, the solution was diluted to 100 c.c. by addition of more carbon disulphide and the mixture well shaken.

Two portions of 25 c.c. of the solution measured by means of a pipette (using a water pump to suck up the solution) were transferred to dry glass-stoppered bottles, and 25 c.c. of the bromine solution in carbon disulphide, measured in the same way, added to each. The bottles were set aside in a dark cupboard for fifteen minutes.

* Great care is necessary in this operation owing to the very harmful nature of bromine and its vapour. It is also extremely important to notice that carbon disulphide is a dangerously inflammable liquid.

Blank Experiment.—25 c.c. of the bromine solution in carbon disulphide were placed in a glass-stoppered bottle and treated with approximately 10 c.c. of the solution of potassium iodide. Decinormal sodium thiosulphate solution was then run in from a burette. The mixture was vigorously shaken after each addition of thiosulphate, since much of the iodine liberated by the bromine remains dissolved in the carbon disulphide. When most of the colour of the liquid was discharged a few drops of starch solution were added, and the sodium thiosulphate added one drop at a time, the mixture being vigorously shaken as before, until the blue colour disappeared.

Volume of N/10 $\text{Na}_2\text{S}_2\text{O}_3$ required (1) 25.3 c.c.
(2) 25.2 „

Mean 25.25 „

Test Experiments.—The solutions of bromine containing the oil were then treated in the same manner.

Volume of N/10 $\text{Na}_2\text{S}_2\text{O}_3$ required (1) = 20.1 c.c.
(2) = 20.3 „

Mean 20.2 „

The bromine absorbed by the oil is thus equivalent to $25.25 - 20.2 = 5.05$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

1 c.c. N/10 $\text{Na}_2\text{S}_2\text{O}_3 = 0.008$ gram bromine

$\therefore 5.05$ c.c. N/10 $\text{Na}_2\text{S}_2\text{O}_3 = 5.05 \times 0.008 = 0.0404$ gram bromine.

Weight of oil used for each experiment

$$(25 \text{ c.c. of } 100 \text{ c.c.}) = \frac{3.92}{4} = 0.98 \text{ gram}$$

$\therefore 0.98$ grams of oil absorbed 0.0404 grams bromine.

$\therefore 100$ „ „ „ 4.1 „ „

In carrying out a bromine absorption it is important to notice that the mixture must be kept in a *dark* place for fifteen minutes. It is known that the action of halogens on various substances is greatly influenced by light, and since it is impossible to arrange conveniently to carry out these determinations in light of equal intensity on different occasions, it is usual to carry out such absorptions in the absence of light.

Similarly, the solution of bromine in carbon disulphide is

kept in a dark place, or in a black bottle, since under such conditions the action of the bromine on the carbon disulphide is reduced to a minimum.

It is essential that at least half the bromine originally taken shall remain in excess at the end of an experiment in order to ensure that the oil is in contact with excess of bromine throughout the whole absorption. If this is found not to be the case in any determination, a fresh experiment should be undertaken, using a larger amount of the bromine solution.

For effect of light, temperature, dilution, excess of bromine, etc., in such experiments, see *Fourn. Soc. Chem. Ind.*, 1888, page 64.

It will be noticed that in the bromine absorption described above, no determination is made of the amount of bromine that is used in *substitution*, with consequent liberation of hydrogen bromide. A method is described for effecting this determination (*Fourn. Soc. Chem. Ind.*, 1900, page 176), in which use is made of the fact that hydrobromic acid liberates iodine from potassium iodate.

For typical bromine absorptions, see page 324.

Alternative Method for Comparing the Olefine Content of Oils.—An approximate comparison of the olefine content of two samples of oil may also be made by determining the amounts of potassium permanganate decomposed by equal quantities of the oils.

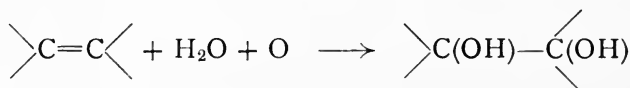
Equal weights of the two samples are placed in similar glass-stoppered bottles, and treated with a measured volume of a standard potassium permanganate solution and dilute sulphuric acid.

The mixtures are frequently shaken, the amount of shaking being as nearly as possible the same in each case. The excess of potassium permanganate remaining in solution is then determined by running in a solution of ferrous ammonium sulphate containing sulphuric acid.* From the difference in the amount of the ferrous ammonium sulphate solution required in a blank and in the test experiment for a certain volume of potassium permanganate solution, the amount of potassium permanganate used for the oxidation of the olefines in a given weight of each oil is found, and from this a comparison of their olefine content obtained.

By the action of potassium permanganate, ethylenic

* It will be recalled that in potassium permanganate-iron titrations it is usual to run the permanganate into the ferrous iron solution.

compounds are first converted into glycols (dihydric alcohols) (see page 13), which are further decomposed by the prolonged action of the potassium permanganate—



Solutions required—

Decinormal potassium permanganate solution.

3.16 grams of the finely-powdered salt are transferred to a beaker, treated with water, the solution poured off into a litre flask, and the process repeated until all the salt has dissolved. The solution is then diluted to 1 litre, after which it is well shaken.

Ferrous ammonium sulphate solution—

10 grams of the salt are transferred by means of a funnel to a 250 c.c. flask, dissolved in water containing some dilute sulphuric acid and the solution diluted to 250 c.c., and well shaken.

For the experiment employ 5 grams of each sample of oil, add 25 c.c. of N/10 potassium permanganate, and 25 c.c. dilute sulphuric acid. Allow to stand for 10 minutes with frequent shaking, after which the ferrous ammonium sulphate is run in until the potassium permanganate is decolorized, the solution being well shaken after each addition.

CHAPTER XI

THE DISTILLATION OF BITUMINOUS SHALES

ONE of the first recorded distillations of a bituminous shale was carried out by the French chemist, Laurent, in 1830. From the products obtained he was able to separate a mixture of solid hydrocarbons of the paraffin series.

Between the years 1835 and 1845, several patents were granted to Selligie, dealing with the manufacture of paraffin wax from bituminous deposits, and by the end of that period the processes of shale distillation, purification of paraffin wax and lubricating oils, as well as the utilization of the by-products, such as ammonia, seem to have been fairly thoroughly worked out and tested.

The shale-oil industry originated, therefore, in France, where it is still carried on to a large extent, being, however, principally confined to four Departments, *Saône-et-Loire*, *Allier*, *Puy-de-Dôme* and *Basses Alpes*. The principal deposits of shale are found in the first two Departments. At the present time the French shale-oil industry is not so flourishing as that of Scotland, which was founded about twenty years later by Dr. James Young.

The first processes devised and patented by this chemist consisted in "obtaining paraffin oil, or an oil containing paraffine, and paraffine from bituminous coals" by slow distillation. One of the coals used at the commencement was the mineral known as Boghead coal, or Torbanehill mineral, which after a time, however, became exhausted. Since then the oil and paraffin wax obtained in Scotland have been derived from the shales of the coal measures, those of *Linlithgow* and *Midlothian* furnishing the principal supply.

Other deposits of bituminous shales are to be found in *Servia*, *New South Wales*, *Canada* and *South Africa*. The industries connected with these deposits are, however, of relatively small importance.

The shale itself is dark-coloured, and usually has a specific

gravity of about 1.75. It may contain 70 to 80 per cent. of mineral matter, and in consequence of this it is not at all surprising that it does not "coke" on heating, but retains more or less its original appearance.

Since the commencement of shale distillation in Scotland, about 1850, a great many alterations and improvements in the retorts have taken place. The same is true of the methods of heating, of charging and discharging, of removal of the products of distillation, of recovering the bye-products, *e.g.*, ammonia, and in increasing the yield of this gas without diminishing that of the hydrocarbons. Into all these processes we cannot enter very deeply here, but would refer the reader to Redwood's "Treatise on Petroleum," 1913 edition, vol. ii.

Some account of the more important details connected with shale distillation must, however, be given.

In the very early days of the industry, the distillation was carried out in horizontal retorts, similar to those still largely employed in the manufacture of coal gas. These were heated by the combustion of the heavier oils and paraffin wax obtained in the distillation, since at one time there was little demand for these products which at the present day are so valuable.

When a demand arose for the solid paraffins, however, the distillation was carried out in vertical retorts heated by producer gas and the uncondensable gases evolved during the distillation; in this way the vapours were conducted more quickly away from the heated area, and the "cracking" of the higher-boiling fractions diminished. The retorts were charged and discharged continuously. (Compare distillation of coal, page 218.)

At a somewhat later date, steam was introduced into the vertical retorts, by means of which the removal of the products of distillation was accelerated, an effect which has since been obtained by diminishing the pressure in the retorts.

In some cases the use of steam has caused an enormous increase (in one case about 25-30 per cent.) in the amount of liquid distillate obtained. The introduction of the steam has since been found to serve several other useful purposes. It is always introduced at the base of the vertical retort, where it comes into contact with the spent shale which collects at the bottom and which can be periodically (or continuously) removed. The shale is introduced at the top by means of a hopper. The spent shale contains 9-14 per cent. of carbon which, in contact with the steam, produces water-gas. The

heat evolved in this decomposition helps to maintain the temperature of the retorts. The combustion of this spent shale is often facilitated by the introduction of air, simultaneously with steam, into the retorts.

The steam also removes the ammonia, which is always produced, more quickly from the heated area, thereby preventing or diminishing its decomposition.

Not only does the introduction of steam affect the yield of ammonia in this indirect manner, but it actually *causes* the production of a considerable amount, since the spent shale at the bottom of the retort still contains nitrogen which would otherwise have been lost. It was shown by Young and Beilby that shale from which all volatile matter had been completely removed by distillation, could still be made to yield ammonia when heated to a high temperature in a current of steam.

SHALE OIL AND THE PRODUCTS OF ITS FRACTIONAL DISTILLATION.

On the average a Scotch shale will yield about 20-50 gallons of crude oil, and about 30-60 pounds of ammonium sulphate per ton.

With the gas and the ammoniacal liquor we need not further concern ourselves, but the crude oil must be dealt with at some length.

It usually possesses a dark green colour, a specific gravity of 0.860 to 0.890 and is very viscous owing to the large quantity of solid paraffin hydrocarbons which it contains. That obtained from the newer types of retorts has a setting-point of about 32° C.

It contains about 70-80 per cent. of members of the paraffin and olefine series, certain bases derived from pyridine and also cresols and phenols in relatively small amounts. Its odour differs entirely from that of coal or wood tars.

For a description of the various types of distilling plant used in connexion with the shale oil industry the reader is referred to a larger treatise on the subject.

The crude oil is first redistilled under ordinary pressure. As soon, however, as the water and any ammonia which the oil may still contain, as well as a very low-boiling mixture of hydrocarbons of sp. gr. 0.740, have passed over, superheated steam is introduced into the still which is all the time heated from below.

By this means distillation is accelerated and the decomposition of the valuable solid paraffins reduced to a minimum. As the temperature of distillation rises the quantity of steam is increased and its passage continued for two or three hours after distillation (which is conducted till only coke remains in the retort) has ceased.

The whole of the oily distillate with the exception of the low-boiling fraction already referred to is collected in one tank. This is known as *once run oil*. After separation of the water, its purification is effected by agitation with sulphuric acid of sp. gr. 1.72 by means of a stream of compressed air, at a temperature just high enough to prevent the solidification of the higher paraffins, *i.e.* about 50° C. After settling, the oil is run off from the "acid-sludge" into soda-lye with which it is vigorously agitated as before. Sulphuric acid and phenols are thereby removed.

The purified once run oil is now submitted to a careful fractional distillation, steam being introduced as before, as soon as the more volatile portions have been removed.

Three principal fractions are obtained, and are run into separate tanks:

- (i) "green naphtha" with a sp. gr. up to about 0.770
- (ii) "burning oil" " " " " 0.850
- (iii) "green oil."

After a further washing with sulphuric acid and caustic soda the green naphtha is redistilled, when that portion of the distillate having a specific gravity not greater than 0.760 is collected separately and designated "shale spirit" or "shale naphtha." This forms a very volatile, inflammable liquid which is colourless and has a somewhat more pronounced odour than the low-boiling fractions obtained from petroleum.

It consists of a mixture of hydrocarbons of the paraffin and olefine series, the latter forming about 60 per cent. of the whole. The shale naphtha is sometimes submitted to yet another fractional distillation whereby it is separated into (i) gasoline (up to 0.680 specific gravity), (ii) motor spirit (up to 0.718 specific gravity, (iii) heavy spirit (up to 0.750 specific gravity).

Refining of the Higher Boiling Fraction of Shale Oil—(a) The Burning Oil.—The second fraction obtained on distillation of the *once run oil* is submitted to a further treatment with 0.5 to 0.75 per cent. of its volume of concentrated sulphuric acid and allowed to settle; the acid which finally separates is used again for the purification of "once run light oil."

After agitation with caustic soda solution the oil is fractionally distilled when a certain amount of shale naphtha passes over at the commencement. That fraction having a specific gravity of from 0.840 to 0.850 is used as burning oil, while the portions of higher density yield about 5 to 10 per cent. of crude paraffin wax, the so-called "soft paraffin scale."

(b) **The Heavy, or Green Oil.**—(This is not to be confounded with the green or anthracene oil obtained in the distillation of coal tar.)

This fraction contains the bulk of the paraffin wax and is set aside for several days, when large quantities of solid paraffins are deposited. These are separated in filter presses and then submitted to great pressure, by means of which the bulk of the oily impurities are removed and a product known as "hard scale" obtained. The expressed oil, as well as in some cases the original heavy or green oil, is then cooled by means of ammonia or ether refrigerating machines, when a further deposit is obtained. This, when obtained from the expressed oil, is known as soft scale.

At one time the crude "scale" was purified by means of three successive crystallizations from some low-boiling hydrocarbon such as benzene or light petroleum.

The deposited solid paraffins were freed from solvent, from dissolved oily matter and less pure paraffin hydrocarbons by submitting them to pressure; the solvent was of course recovered as far as possible. A further purification was effected by decolorization with animal charcoal.

This very expensive method has now, however, been almost entirely superseded by the so-called "sweating process" which has also found much application in the purification of the paraffin wax obtained from petroleum. For a full description of this process reference should be made to standard works dealing with the shale industry.

The essential details of the process consist, however, in submitting the crude paraffin scale to a temperature at which the greater portion of the impurities present melt and can be run off. The temperature is usually about 80° F. at the commencement, and is gradually raised till a temperature a few degrees below that at which the purified wax should melt is obtained.

In one of the new methods the crude scale is melted and allowed to solidify in shallow iron trays containing water and provided with horizontal diaphragms of wire gauze. These are supported one above the other in a brickwork chamber

which can be heated by means of steam pipes. When solidification has proceeded to the desired extent, the water is run off leaving the cake of paraffin supported on the wire gauze.

Heat is then gradually applied and the sweating continued until the melted paraffin flowing out from the trays is found to solidify at 116° F.

The residual paraffin wax obtained in this way is found to be much harder and to possess a higher melting point than the original crude scale. It is sometimes submitted to a second purification by the same process.

The oily runnings consisting of the lower-melting paraffins along with certain liquid hydrocarbons are allowed to solidify and are again submitted to the sweating process, by means of which a certain amount of hard paraffin wax may be recovered.

It should be mentioned, however, that in the case of *all* the paraffin wax resulting from the sweating process, whether it has been once or twice melted, a final purification with animal charcoal or with fuller's earth is necessary. This treatment removes coloured impurities; the decolorizing agent is afterwards separated by passing the melted wax through filter presses.

The following statistics taken from Martin's "Industrial Chemistry, Organic" (Crosby Lockwood and Son), and dealing with the shale industry will be of interest.

In 1909 three million tons of Scotch oil shale were distilled yielding 280,000 tons of crude oil and 57,000 tons of crude ammonium sulphate. On redistillation the crude oil yielded—

85,000 tons of illuminating oil.

16,000 tons of motor spirit.

46,000 tons of oil suitable for gas manufacture.

40,000 tons of lubricating oil.

25,000 tons of paraffin wax.

OIL-SHALE DISTILLATION ON A LABORATORY SCALE.

About one kilogram of the finely-powdered shale is placed in the iron retort indicated in Fig. 35, which is connected with a reservoir B and one or more wash bottles, the last-named containing dilute sulphuric acid.

The shale is introduced at the end of the iron retort, which is about 50 cm. long and 8 cm. internal diameter, by

unscrewing the cap A. This is fitted with a brass tube which may be connected with a manometer, as indicated in the figure, by means of which any increase in pressure which might conceivably occur owing to some temporary obstruction, may be at once detected. This tube serves, however, under certain conditions for introduction of steam. In such cases the reservoir and wash bottles should be cooled in water.

After the retort has been tightly closed* the heating is commenced by means of a double row of small Bunsen gas jets which may at once be turned full on. Excessive loss of heat by radiation from the large surface of the retort may be prevented by enclosing it temporarily within movable asbestos sheets.

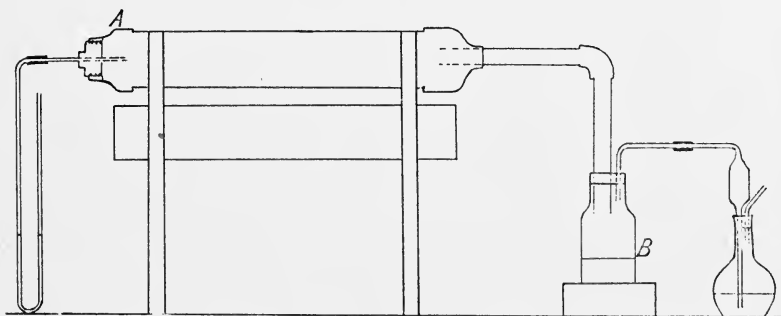


FIG. 35.—Retort for laboratory distillation of shales.

Distillation of the shale oil begins very shortly and a dark brownish green liquid, accompanied by about an equal volume of water, collects in the reservoir which should be well-cooled in a trough of water. A certain amount of the more volatile oil passes over along with ammonia gas into the sulphuric acid wash bottle. Large quantities of inflammable, unpleasant-smelling gas† escape from these wash bottles and should be conducted away to a good draught. It is important that the draught should be efficient, otherwise an accumulation of inflammable gas may occur and give rise eventually to an explosion.

The presence of unsaturated hydrocarbons in the evolved gases can be detected by bubbling them through dilute potassium permanganate which is quickly decolorized, hydrated manganese dioxide being precipitated.

* It is advisable to place a small quantity of a mixture of powdered graphite and lubricating oil on all threads before screwing up.

† For methods of determining the composition of this gas text-books on Gas Analysis should be consulted.

The gases also produce a brown precipitate when bubbled through an ammoniacal solution of cuprous chloride, indicating the presence of acetylene (see page 87).

When distillation ceases the dark-green upper oily layer in the reservoir is separated from the ammoniacal aqueous liquor as completely as possible.* Any oil which has collected in the wash bottle should be separated from the acid and added to the main bulk.

The volume of oil obtained is measured. This is then placed along with a few small pieces of porous tile in a capacious flask of such a size that when containing the oil only about $\frac{1}{4}$ to $\frac{1}{3}$ of its volume is occupied. A water condenser fitted with an adapter, filter flask and rubber tube as in Fig. 40, page 206, is connected with the flask, which is then gently heated over a free flame kept in constant motion.

Until all water and dissolved ammonia contained in the oil are expelled the flask should be heated only very gently, since a considerable amount of frothing will occur; hence the necessity for using a large flask. The temperature of the vapours which distil is noted by means of a thermometer.

After the removal of the water the distillation will proceed very smoothly. An air condenser should be used when the temperature reaches 100°C . When the thermometer indicates 170° the receiver may be changed and the following fractions collected:—

- (i) up to 170°
- (ii) 170° – 230°
- (iii) 230° – 270°
- (iv) above 270°

A very large proportion of the original shale oil will be found to be non-volatile below 300° . This consists largely of high-boiling solid paraffin hydrocarbons of the series $\text{C}_n\text{H}_{2n+2}$.

Examination of the Various Fractions.—The fraction distilling below 170° contains a considerable amount of ammoniacal liquor. This is removed by means of a tap funnel and the residual oil is washed two or three times with dilute

* The ammonia contained in this liquor and that combined with the dilute sulphuric acid in the wash bottle may be obtained by adding excess of lime or sodium hydroxide in order to decompose the ammonium salts and then distilling. The evolved gas is best absorbed in sulphuric acid from which the ammonium sulphate may be obtained on concentration. For a method of estimating the amount of ammonium sulphate obtainable from a given weight of shale see page 191. As previously stated on page 184, the yield of ammonia is increased by the introduction of steam into the retort.

sulphuric acid by which means any other basic constituents are also removed. After a further washing with dilute sodium hydroxide, followed by water, the oil is well dried over calcium chloride and redistilled. If it still possess a very unpleasant odour it may be allowed to stand in contact with moist lead hydroxide $Pb(OH)_2$ or with litharge PbO whereby certain sulphur compounds may be removed.

The purified first fraction contains very large quantities of unsaturated hydrocarbons of the ethylene or olefine series C_nH_{2n} .

An instructive series of experiments may be carried out with this product, *e.g.* the percentage of unsaturated hydrocarbons it contains may be determined according to the methods described in Chapter X.

Another portion of the same specimen may be shaken with hydrogen in presence of a colloidal palladium solution till absorption ceases (see page 247). The oil may then be recovered, dried and a second determination of its olefine content carried out, when the amount of bromine absorbed will be found to be very much less; it may have fallen even to zero.

It will probably be noticed that, after the treatment with hydrogen, the odour of the oil has altered. Its behaviour with ordinary concentrated and with fuming sulphuric acid and also with neutral, dilute potassium permanganate solution before and after hydrogenation should be noted.

Instead of carrying out the hydrogenation by means of Skita's method, a portion of the "shale naphtha" may be passed in the vaporous condition mixed with hydrogen through a tube containing freshly reduced nickel and the properties of the resulting product compared with those of the original specimen (see page 251).

Separation of the Shale Phenols.—The second and third fractions boiling from 170° to 230° and from 230° to 270° respectively should be separately extracted with successive small quantities (10–20 c.c.) of ten per cent. sodium hydroxide solution.

When in each case a portion of the latest extract ceases to give an appreciable turbidity on acidification with sulphuric acid, the alkaline extracts from each fraction are united and *carefully* rendered *slightly* acid by the slow addition of commercial concentrated sulphuric acid (see under "Separation of the Constituents of Carbolic Oil," page 240).

The dark-coloured oily layer of phenols which separates is

removed from the *clear* aqueous liquid by means of a tap funnel, dissolved in a little ether, the solution dried with anhydrous sodium sulphate, the ether evaporated and the residual oil distilled.

If the quantity obtained be sufficient it may be submitted to a further distillation, using a fractionating column. In either case the readings of the thermometer should be carefully noted and any distillate coming over while the thermometer remains constant should be collected separately.

The odour of the distillate should be noted as well as its behaviour towards (i) aqueous ferric chloride solution, (ii) bromine water (see page 207).

The amount of phenols present may be estimated by acidifying the sodium hydroxide extract, obtained from a known volume of oil, in a flask with a long graduated neck. The phenols float on the surface of the acid liquid and their volume may be read off.

The presence of unsaturated hydrocarbons in those portions of the second and third fractions which are insoluble in sodium hydroxide should also be tested for.

Estimation of the Amount of Ammonium Sulphate obtainable from Shale.—For this estimation two wash bottles containing dilute sulphuric acid and cooled in water are attached to the reservoir B. One drop of methyl orange is added to the contents of each wash bottle. The shale (1 kilogram) is heated in a current of steam, until no more oil distils over. The contents of the reservoir and the two wash bottles while still warm are transferred to a large separating funnel and thoroughly mixed together, after which the solution should still be strongly acid. After allowing to stand for a short time the lower aqueous layer may be run off into a litre graduated flask and the oil washed several times with some warm dilute sulphuric acid, the washings being added to the contents of the litre flask.

When cold, the solution is diluted to 1 litre and the amount of ammonium sulphate estimated by boiling 50 c.c. of the solution with excess of sodium hydroxide solution and passing the ammonia evolved into 50 c.c. of seminormal sulphuric acid. (For details of the experiment, see text-books on Quantitative Analysis.)

From the amount of sulphuric acid neutralized the amount of ammonium sulphate is calculated as follows:—

1 c.c. $N/2H_2SO_4 = 0.0245$ gram $H_2SO_4 = 0.033$ gram $(NH_4)_2SO_4$; hence the amount of ammonium sulphate in 1

litre of the solution is found. This is the ammonium sulphate produced from the ammonia during the distillation of the oil. If the distillation in the current of steam be continued after all the oil has been driven off from the shale, a further quantity of ammonia is obtained.

This distillation should be continued until the gas leaving the reservoir B ceases to show an alkaline reaction to litmus paper, when the wash bottles are temporarily disconnected. The contents of the reservoir are then mixed with the solutions from the wash bottles, any oil present being separated as before, and the solution diluted to one litre. The ammonium sulphate in the solution is estimated as described above.

Instead of estimating separately the amount of ammonium sulphate produced during the distillation of the oil and that produced after all the oil has been removed, the two solutions of ammonium sulphate may be united and one estimation of the ammonia carried out.

In fact it is generally preferable for the heating and passage of steam to be continued without interruption until no more ammonia is produced; the washings being then diluted to two litres, if necessary. The results should be expressed in gallons of crude oil and pounds of ammonium sulphate produced per ton of shale.

CHAPTER XII

THE "CRACKING" OF HEAVY OILS

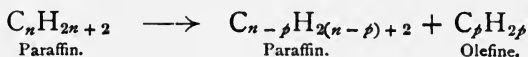
IN this connexion we have to deal with the decomposition by heat of hydrocarbons of high molecular weight into simpler substances.

It is generally believed that the substances obtained in the fractional distillation of a crude oil on a large scale are not necessarily identical with those present in the oil before distillation, but that a certain amount of decomposition takes place even in such a simple process as this. The object of all "cracking" operations is to augment this decomposition.

The fact that a high temperature of distillation tends to increase the amount of the more volatile constituents of the distillate is said to have been discovered through the accidental superheating of an oil still at Newark, New Jersey, in 1861.

An important investigation into the subject was, however, undertaken by Thorpe and Young in 1871. (*Proceedings of the Royal Society*, 1871, vol. 19, 37 and 1873, 21, 185.)

These investigators found that if solid paraffin wax is repeatedly distilled under pressure from one limb of an inverted V-shaped tube to the other, a liquid distillate is eventually obtained, part of which boils below 100° C., comparatively little gas being produced in the process. They showed that in addition to paraffin hydrocarbons, olefines were also obtained, the decomposition being represented by the general equation—



Thus the hydrocarbon $\text{C}_{15}\text{H}_{32}$ could give the paraffin $\text{C}_{10}\text{H}_{22}$ and the olefine C_5H_{10} or the paraffin C_5H_{12} and the olefine $\text{C}_{10}\text{H}_{20}$ or C_7H_{16} and C_8H_{16} , etc.

In a series of experiments Thorpe and Young distilled 3.5 kilograms of a shale paraffin wax, of melting point 46° C. and obtained 4 litres of liquid distillate, which on fractionation

was found to be composed of hydrocarbons boiling as follows:—

Below 100° C.	0·3 litres
100°–200°	1·0 „
200°–300°	2·7 „
	<hr/>
	4·0 „

These distillates were fractionated, and the lighter portions obtained were shown to consist of approximately equal quantities of paraffin and olefine hydrocarbons. Normal paraffins from pentane to nonane were isolated from these distillates; whilst on treatment with bromine several addition products were obtained. Practically all of these were shown to be identical with the dibromo addition-products of certain well-known olefines.

The decomposition of hydrocarbons by heat was also investigated by Armstrong and Miller, who published a paper on "The Decomposition and Genesis of Hydrocarbons at High Temperatures" ("Transactions of the Chemical Society," 1886, vol. 49, 74). These investigators called attention to the preponderance of unsaturated hydrocarbons in the products obtained by "cracking" oils.

A certain amount of cracking of heavy oils has been carried on for a long time in the course of their distillation, in order to increase the kerosene fraction of the oil. This is accomplished by allowing the condensed liquid to fall back into the hot still. From the "cracking" sound, which accompanies some of these operations the process derives its name. The production of "oil gas" by dropping oil into a red-hot retort has also been practised for a considerable time, and the process is now largely employed in the manufacture of "carburetted water gas."

Various forms of stills and retorts for effecting these objects are described in Redwood's "Treatise on Petroleum," vol. ii. pp. 8–13.

One of the drawbacks to "cracking" crude oils in order to increase the amount of the lighter fractions is that during the purification a larger amount of sulphuric acid is required, owing to the increased amount of olefine hydrocarbons present as the result of the "cracking" process.

Another objection to the cracked product is the objectionable smell often associated with it, which is also probably due to the preponderance of unsaturated hydrocarbons. The removal of smell by hydrogenation is well illustrated by

employing a cracked oil in the Paal-Skita hydrogenation process: see page 247).

Cracking for Light Oils.—During the last few years cracking processes for the production of light oils have received a large amount of attention, for it is obvious that if petrol can be made successfully from paraffin oil, which costs about eight-pence per gallon, the process would be extremely valuable.

In the Cowper-Coles process (English Patent No. 27945 of 1906) the vapour of the heavy oil is conducted through a series of small heated metal tubes whereby the flash point of the oil is reduced from about 120° F. to about 16° F.

In the Noad and Townsend process (English Patent No. 13675 of 1908) the liquid oil and water, in the proportions of approximately two parts of oil to one of water, are dropped into a heated retort filled with scrap iron maintained at a temperature of about 900° F.

The vapours from the retort are condensed and the volatile spirit separated by fractional distillation, the heavier oil being returned to the reaction chamber for further treatment. It is claimed that in this process practically the whole of the oil is converted into volatile spirit and only a low percentage of permanent gas and residual carbon is obtained.*

In the Ellis process (English Patent No. 25631 of 1913) (*Journ. Soc. Chem. Ind.*, 1913, 1098) the heated oil is sprayed into contact with granular refractory material contained in a chamber which is capable of withstanding high pressures. At the same time air is injected into the chamber in sufficient quantity to effect the combustion of a small proportion of the oil vapour. Owing to the high temperature and pressure produced much of the remaining oil is "cracked," the products being separated in a series of condensing chambers.

In the Planes and Thompson process (English Patent Nos. 5245 and 21273 of 1913) hydrogen or purified water gas is passed through the purified heavy petroleum heated under pressure in the presence of finely divided nickel, immersed in the liquid. The products are separated by suitable fractionation.

Other processes are referred to in *Journ. Soc. Chem. Ind.*, 1913, pages 203 and 861.

"Cracking" for Oil Gas.—As previously mentioned, another branch of "cracking" is met with in the production of the so-called oil gas. In this case the oil is allowed to drop into

* The formation of a large volume of gas and the deposition of an inconvenient amount of carbon are obviously undesirable during cracking operations, the object of which is to produce volatile liquid hydrocarbons.

a red-hot retort and is practically completely converted into so-called "permanent gas," *i.e.* gaseous material which does not condense on cooling. Only a small quantity of tar is produced at the same time, and if the oil is allowed to enter the retort at the proper rate, the amount of volatile oils produced is insufficient to deposit liquid on cooling, that is, these substances are present as unsaturated vapours (see page 91).

This process is largely made use of for "enriching" water gas by converting it into the so-called carburetted water gas. This serves to increase the luminosity of the water gas, since the gaseous products derived from the oil are rich in unsaturated hydrocarbons, which burn with a luminous flame. Carburetted water gas is largely used for mixing with ordinary coal gas.

The process for making gas from oil dates back to 1815, when a patent was granted in this country for its manufacture.* Oil gas is chiefly used in railway carriage lighting and for general purposes in places where coal gas is not available.

A typical oil gas producer is shown in the diagram Fig. 36. This plant, known as Mansfield's patent oil gas producer, is apparently suitable not only for making gas from petroleum oils, but also from fatty oils and even fats.

The method of making the gas is described by the manufacturers as follows:—

"A fire is lighted in the firebox, either wood or coal being used, and a steady heat is maintained until the retort, which is shown suspended inside the producer fireclay linings, is heated to redness. The progress of this heating may be watched through the sight plug. It will be noticed that the top of the retort is fitted with a groove which is filled with lead. The object of this is to make an automatic joint with the connecting pipes to the gasholder. As soon as the retort is sufficiently hot for gasmaking, the lead in this groove is melted and the connecting pipe, which is called the "bonnet," sinks into the molten lead and an automatic gas-tight joint is made. The other end of the bonnet is sealed in the same manner in water. When gasmaking is finished, and before the heat is lowered, the bonnet is lifted out of the molten lead and left resting on the top of the retort. After cooling,

* In connexion with the production of oil gas most stress is laid on the yield of gas per gallon of oil and the candle power of the gas obtained. See paper by J. F. Tocher, *Journ. Soc. Chem. Ind.*, 1894, p. 231, in which tables are given showing the nature of the products from various hydrocarbons and oils. See also Typical analyses, page 326.

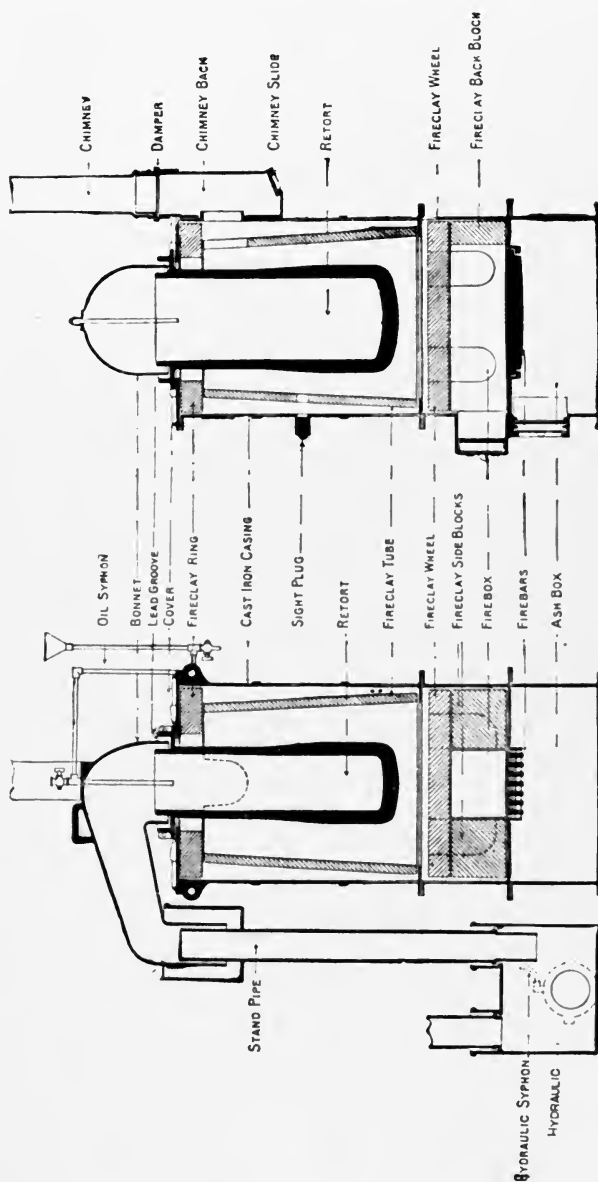


FIG. 36.—The Mansfield oil gas producer.

access can then be gained to the inside of the retort, for cleaning purposes.

"Oil, stored in a suitable tank in any part of the building, is led to the oil syphon of the producer by means of a pipe. A small cock attached to the end of the pipe regulates the flow of oil which is permitted to run in a fine stream into the funnel of the oil syphon. The oil syphon is simply a U-shaped pipe, which permits the oil to flow through it into the retort but will not allow the gas to come back where the oil enters. In this manner a constant stream of oil is poured into the red-hot retort. As soon as the oil reaches the hot retort, it is immediately converted into a permanent gas. As the newly-made gas cannot escape where the oil enters, it rises into the bonnet and passes down the standpipe into the hydraulic main, which is partly filled with water to the level of the overflow. It is made to bubble through this water and then passes through the connecting pipes into the gasholder where it is stored. The object of this hydraulic main is to permit the gas to pass from the retort to the gasholder, and to prevent its return from the gasholder to the retort. The gas made in this manner is "fixed," will not condense, and cannot be converted into oil again."

CRACKING OF OIL ON A LABORATORY SCALE.

The principle of "cracking" of oils may be illustrated by means of the apparatus shown in the diagram Fig. 37.

Paraffin oil is allowed to flow from the burette A, at the rate of about one drop per second into the glass tube B, and thence into the iron tube C. It then passes into the wider iron tube D (about 90 cm. long and 2.5 cm. internal diameter) which is packed with pieces of broken porous tile and heated to dull redness in a combustion furnace.

To the other end of this tube D a piece of iron tube E similar to C is fixed by means of a reducing nipple, and this then passes through a cork into a bottle F, which serves to catch heavy oil, unchanged paraffin and some light oil. Uncondensed vapours and gases pass from this bottle into a water condenser G. A filter flask H is fitted to the end of this condenser by means of an adapter, and a wash bottle J is attached to the side tube of the filter flask. The gas and any vapour which is not condensed then passes up a tower K filled with moistened glass balls, and the gas escaping from this tower may be burnt or passed into a fume duct. The

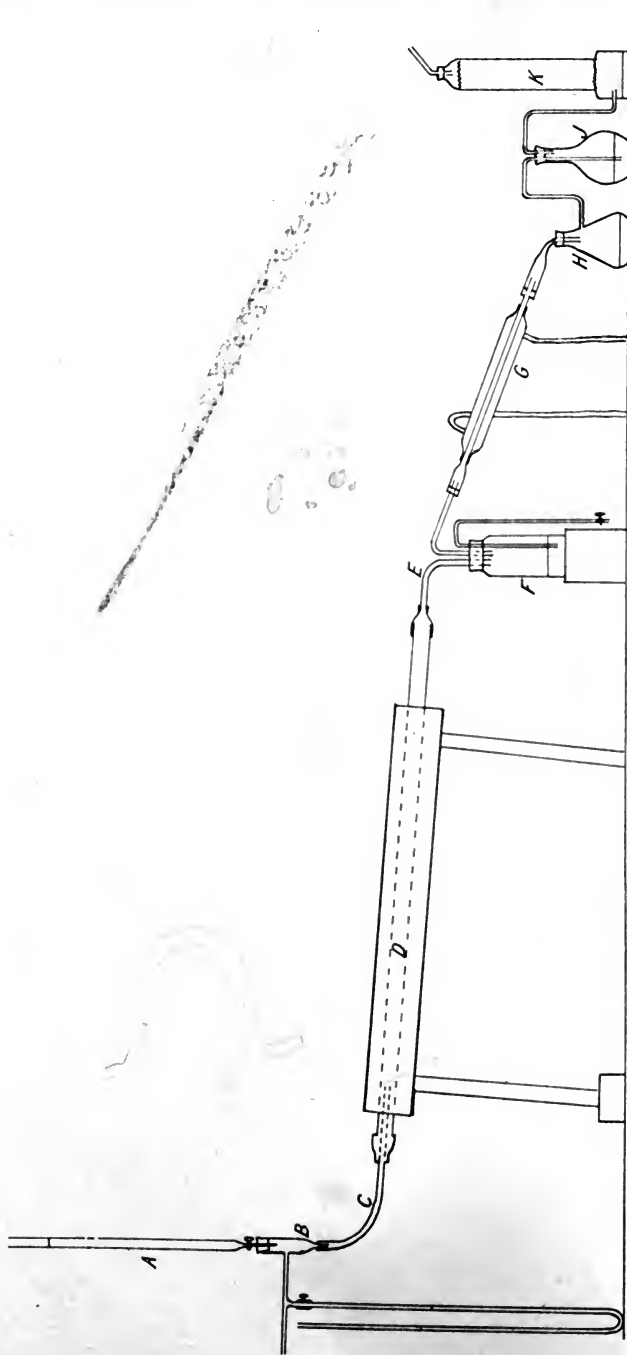


FIG. 37.—Apparatus for cracking heavy oils.

presence of acetylene and other unsaturated hydrocarbons in this gas may be shown in the usual manner.

Before an experiment is started the air in the apparatus is displaced by means of a stream of coal gas passed into B. The pressure in the apparatus is denoted by means of the water manometer attached to B.

500 c.c. of paraffin oil should be passed through the apparatus. The volume of the distillates collected in each receiver should be noted, and their densities, flash points, range of distillation, olefine content, etc., should be compared with those of the paraffin before "cracking."

By making a slight alteration in the apparatus, water may be allowed to pass into the tube simultaneously with the paraffin and the effect of the presence of steam on the course of the reaction can thus be investigated. The tube may also be filled with scrap iron, nickel or other metal, etc., and the character of the product obtained under different conditions compared.

CHAPTER XIII

PREPARATION OF CERTAIN AROMATIC COMPOUNDS

PREPARATION OF BENZENE.

MIX 20 grams of benzoic acid C_6H_5COOH and 50 grams of well-powdered quick-lime or soda-lime very thoroughly in a mortar. The success of the experiment depends on the dryness of the materials and the intimacy of their admixture.

Place the mixture in a dry round-bottomed flask or boiling tube supported horizontally and connected with a well-cooled water condenser. The flask or tube should be inclined as shown in the diagram Fig. 38, in order that any liquid which condenses shall not flow back on to the heated portion of the tube. On heating, benzene distils over and may be collected in a suitable receiver. It is at first colourless, but if the heating be continued long, a small amount of tar is produced which colours the distillate reddish yellow. Tarry bye-products are often formed in such reactions.

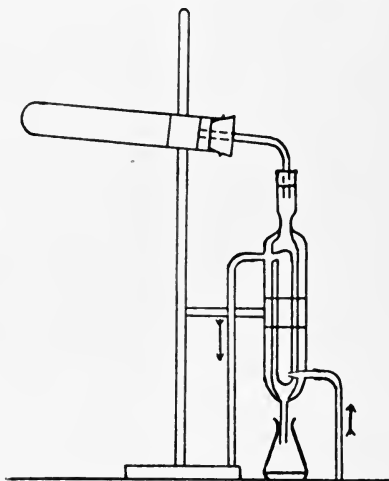
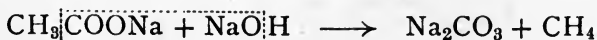


FIG. 38.—Apparatus for preparation of benzene.



Compare—



Add a little anhydrous calcium chloride to the distillate in successive small quantities to remove the water. If the quantity of water be considerable as much as possible should first be removed by means of a small separating funnel. Allow to stand for an hour or so and distil the dried benzene from a small distillation flask. A fragment of tile should be added to the benzene before distillation, and a water condenser should be employed.

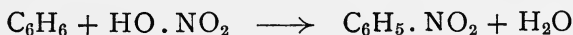
Experiments—

(i) Burn a few drops of the benzene on a crucible lid—note the luminosity of the flame.

(ii) Shake a few drops in a dry test-tube with fuming sulphuric acid and pour into water. The benzene dissolves with the formation of soluble benzenesulphonic acid.



(iii) Shake a few drops in a test-tube with a mixture of concentrated sulphuric acid and nitric acid.



Nitrobenzene is formed, and on pouring the mixture into excess of cold water, is obtained as an oily yellow liquid. Its characteristic odour of bitter almonds should be noted.

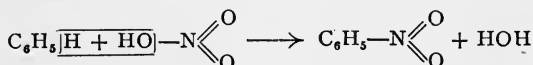
Toluene, xylene, and other aromatic hydrocarbons, but not those of the aliphatic series, also show these reactions.

NITRATION OF AN AROMATIC HYDROCARBON.

Example : Preparation of Nitrobenzene.—60 c.c. of commercial concentrated nitric acid are *gradually* added to an equal volume of commercial concentrated sulphuric acid, and the mixture thoroughly cooled by immersing the flask in cold water and agitating it.*

Fifty grams of benzene are then *gradually* added, preferably from a tap-funnel, in quantities of about 3 to 5 c.c. at a time, the contents of the flask being vigorously shaken and cooled in cold water after each addition.

* The sulphuric acid employed in this preparation serves to absorb the water formed in the reaction.



This would otherwise accumulate, dilute the nitric acid and bring about the cessation of the reaction.

It is important that the shaking should result in a thorough and intimate admixture of the benzene and the acids, otherwise unattacked benzene may accumulate, and at a later stage may enter into reaction with considerable violence. During the course of this preparation flames must be kept at a distance.

As the reaction progresses, oxides of nitrogen are evolved, the temperature rises, an odour of bitter almonds becomes apparent, and nitrobenzene rises to the surface as a yellowish brown oil.

When all the benzene has been added, the contents of the flask are again thoroughly mixed by shaking, and heated on the water bath for about half an hour, during which time the mixture is frequently shaken.

It is then cooled, transferred to a separating funnel, and the lower layer of "spent acids" removed. (This should contain practically no nitrobenzene—test for it by pouring a portion into water and noting that there is no appreciable separation of oil.)

The nitrobenzene remaining in the separating funnel must now be washed free from acid. This is done by shaking up twice with water and removing the nitrobenzene which now forms the *lower* layer. It is then washed once with dilute sodium carbonate solution, and finally again with water.

During the process of washing, any nitrobenzene which does not readily separate may usually be caused to do so by running off the main portion, adding a little more water, and shaking. It will probably be observed that the sodium carbonate wash-liquors are coloured reddish-yellow. This is probably due to the presence of slight traces of trinitrobenzene, $C_6H_3(NO_2)_3$, which is known to give a red colour with aqueous sodium carbonate. Mono- and dinitrobenzenes do not give this colour.

After the last washing with water the nitrobenzene is separated as completely as possible and shaken up in a separating funnel with successive small quantities of anhydrous calcium chloride. The turbid liquid gradually clears, and a saturated solution of $CaCl_2$ separates as the lower layer, and is periodically run off. When no more separates, the nitrobenzene, which still contains water, is allowed to stand overnight in contact with anhydrous $CaCl_2$ in a dry flask.

The yellow liquid is then decanted into a distilling flask which must obviously be scrupulously dry, and distilled, using a long, dry, air condenser. A little benzene may pass over at first, but the temperature quickly rises to 200° . The portion

coming over between 204° and 207° is collected separately. Yield, about 60 grams. B.P. pure nitrobenzene is 206° – 207° .

A certain amount of brown, non-volatile residue remaining in the flask consists of dinitrobenzene, which tends to be formed in larger quantity if the temperature be allowed to rise too high during nitration.

No nitrous fumes should be evolved during the distillation. Their formation indicates that the nitrobenzene has been insufficiently washed. Moreover, the presence of nitric acid during distillation results in the production of more dinitrobenzene.

It should be noted that, as a rule, quite apart from unskilful manipulation, the yields of substances in organic preparations are considerably below the theoretical amounts, owing to the formation of bye-products. For example, in the above case probably only about 75 per cent. of the nitrobenzene demanded by the equation will be obtained.

Since the vapour of nitrobenzene is very poisonous care should be taken to avoid spilling any of the liquid; nitrobenzene residues should not be poured down the sink and so distributed round the laboratory, but rather thrown into an outside drain.

It cannot be too strongly emphasized that this preparation is not to be looked upon as an isolated case, but rather as an example of a method which, with few exceptions, can be applied to the nitration of all aromatic hydrocarbons and many of their more stable derivatives.

Large quantities of nitrobenzene are manufactured for use in the aniline dye industry, and (after conversion into trinitrobenzene) in the manufacture of explosives. Benzene is placed in cast-iron vessels which are fitted with a stirring arrangement and kept cool with water. On allowing a mixture of nitric and sulphuric acids to flow into the vessel the reaction takes place; the nitrobenzene is separated, washed with water, and purified by distillation in a current of steam.

REDUCTION OF AN AROMATIC NITRO-COMPOUND TO THE CORRESPONDING PRIMARY AMINE.

Example: Preparation of Aniline [Aminobenzene, Phenylamine or Phenylammonia] from Nitrobenzene.—Ninety grams of granulated tin are placed in a round-bottomed flask of about $1\frac{1}{2}$ litres capacity, and 50 grams of nitrobenzene added. An upright air condenser about 2 feet long and $\frac{1}{2}$ inch in diameter

is attached, and the mixture warmed on the water bath for a few minutes.

The flask is then removed from the bath and 170 c.c. of crude concentrated hydrochloric acid added down the condenser in successive portions of 5 or 10 c.c., the contents of the flask being vigorously shaken after each addition.

The action soon sets in, heat is evolved and the liquid boils; should the reaction become too violent it may be moderated by immersing the flask in water and shaking. When the whole of the acid has been added and the reaction has slackened somewhat, the flask and its contents are heated

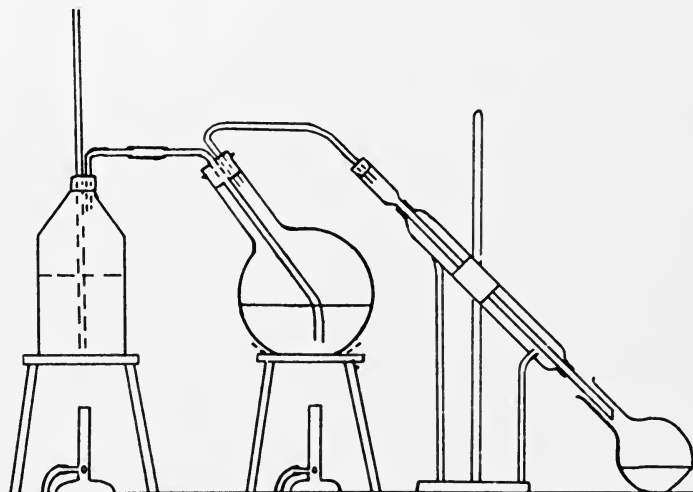


FIG. 39.—Apparatus for distillation in steam.

on the water bath till the odour of nitrobenzene has disappeared. This should be the case when no more oil floats on the surface of the reaction-mixture, owing to its complete conversion into soluble aniline hydrochloride. (On cooling a crystalline double salt of aniline hydrochloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$, and stannic chloride, SnCl_4 , separates.)

As a rule, however, the liquid is only cooled to about 40° and then treated with about 100 c.c. of water followed by a solution of 140 grams sodium hydroxide in 200 c.c. of water, which is added to liberate the aniline from its salt. (What is the precipitate which forms—why does it redissolve?) When after vigorous shaking the mixture possesses a decided alkaline reaction, it is submitted to distillation in steam, Fig. 39.

The inlet tube for the steam, and the outlet tube leading from the flask to the condenser should be of about $\frac{1}{8}$ inch internal diameter. Before introducing the steam the contents of the flask must be heated to about 80° , otherwise too much steam will be condensed, and the volume of the liquid in the steam distillation flask unduly increased. Aniline distils over with the steam,* and separates from the distillate in the form of a colourless oil. When the water which comes over is quite clear the distillation is stopped. The bulk of the

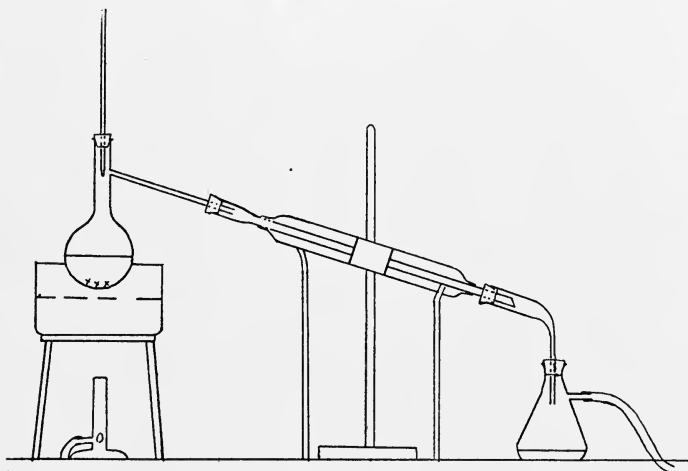


FIG. 40.—Apparatus for distillation of ether, etc.

aniline is at once separated from the watery solution by means of a tap funnel and is transferred to a flask. The aqueous liquor which still contains much aniline is extracted twice with separate quantities of ether which, after separation, are added to the main bulk of the aniline.

The ethereal solution is then carefully shaken in a separating funnel with successive small quantities of *fused* anhydrous potassium carbonate till no more aqueous liquor separates. Compare drying of nitrobenzene, page 203.

The ether extract is now allowed to stand over fused anhydrous potassium carbonate for 24 hours. Anhydrous calcium chloride forms a compound with aniline (also with ammonia), and so cannot be used here.

The ether is then distilled off from the aniline solution in a distilling flask heated on the water bath, and containing a few minute fragments of porous tile.

* See page 95 for theory of steam distillation.

This operation is a dangerous one, and therefore the apparatus indicated in the diagram Fig. 40 *must* be used (see page 77).

The aniline remaining is purified by distillation, using an AIR condenser, and collecting separately that portion of the distillate which boils at 182° – 184° . Pure aniline boils at 183° .

The yield of aniline should be carefully determined and compared with the amount theoretically obtainable.

To a solution obtained by shaking up a few drops of aniline with a little water, a solution of bleaching powder is added, a transient purple colour is produced.

A few drops of aniline are dissolved in a small quantity of dilute hydrochloric acid, the solution well cooled and then treated with a solution of sodium nitrite. On addition of a small quantity of alkaline β -naphthol (β -hydroxynaphthalene) solution, a red azo dye is precipitated (see page 209).

CONVERSION OF A PRIMARY AROMATIC AMINE TO A PHENOL.

Example: Preparation of Phenol from Aniline.—A warm dilute solution of sulphuric acid is prepared by pouring 40 grams of concentrated sulphuric acid into 100 c.c. of water. The acid should be added moderately quickly and the mixture *well stirred during the process*.

Twenty grams of freshly distilled aniline are then slowly added to the hot solution, and the whole stirred vigorously.

After cooling in water, the resulting solution of aniline sulphate is slowly treated with a solution of 17 grams of sodium nitrite in 80 c.c. of water until, on removing a drop of the well-stirred liquid and bringing it into contact with starch potassium iodide paper, a blue coloration is obtained. This shows that excess of nitrous acid is present.

We now have a solution of benzenediazonium sulphate, which is unstable at slightly elevated temperatures. On heating to 40° – 50° for half an hour on the water bath it is converted into sulphuric acid, phenol and nitrogen, which escapes with effervescence.

The mixture is then distilled in steam. Phenol passes over as a colourless oil which, as its quantity diminishes, dissolves in the aqueous liquid which distils. When a few drops of the distillate cease to give a white precipitate with bromine water* the steam may be disconnected. The phenol is obtained from the distillate by means of several extractions

* Phenol and its homologues when treated with bromine water yield white, insoluble substitution products.

with ether; the operation is facilitated if the aqueous phenol solution be saturated previously with common salt.

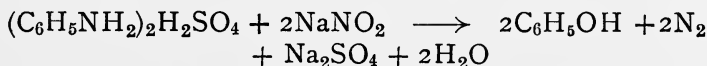
The ethereal solution is dried by shaking with successive small quantities of dehydrated sodium sulphate, running off any aqueous liquor which separates, and finally leaving over dehydrated sodium sulphate for some hours.

The ethereal solution is then poured off from the sodium sulphate and the ether evaporated according to the method and with the apparatus described on page 206.

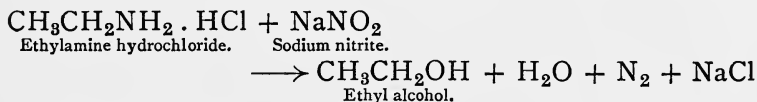
The remaining residue of phenol is distilled using an air condenser and collecting the fraction boiling at 183° , which should solidify on cooling.

The yield as usually obtained is about 15–16 grams.

Equation—

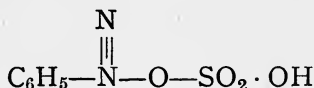


Theoretical Note.—It might be supposed at first sight that the reaction which has just been described is exactly analogous to the well-known reaction between an aliphatic amino-compound and nitrous acid, *e.g.*—



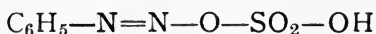
In the course of the reactions of which this last is but a typical example, the formation of intermediate compounds has not been noticed, but when any primary aromatic amine reacts with nitrous acid the extremely important diazonium compounds are first produced and if the preparation be carried out in anhydrous solvents, these compounds can often be isolated, *e.g.* aniline sulphate in absolute alcohol solution and in presence of anhydrous amyl nitrite gives rise to the well-crystallized benzenediazonium sulphate.

When aqueous solvents are employed, as in the foregoing preparation, this substance remains in solution, and on heating undergoes decomposition, yielding phenol, sulphuric acid, and free nitrogen which escapes with effervescence. For reasons which cannot be entered into here, it seems fairly well established that benzenediazonium sulphate has the formula



where one N atom is quinquivalent.

On warming the aqueous solution it undergoes isomeric change into diazobenzene sulphate



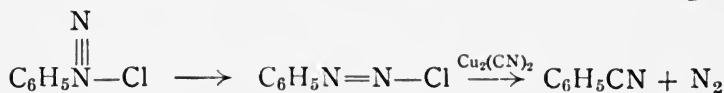
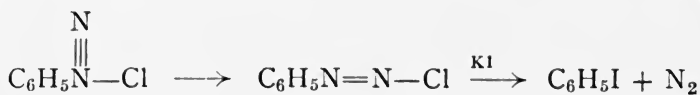
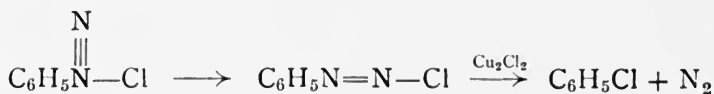
where both N atoms are tervalent. This is unstable and reacts with warm water, giving rise to the products just mentioned.

The diazonium salts (which are to be distinguished carefully from the often coloured diazo-compounds) are colourless crystalline compounds which in the dry condition usually explode on heating. They are readily soluble in water and the solutions of the chlorides form double salts with PtCl_4 and AuCl_3 the composition of which is analogous to that of K_2PtCl_6 , $(\text{NH}_4)_2\text{PtCl}_6$ and KAuCl_4 .

With the calculated amount of moist silver oxide ($\text{Ag}_2\text{O} \cdot \text{H}_2\text{O} = 2\text{AgOH}$) they produce solutions of the corresponding hydroxides some of which have a concentration of —OH ion approaching that of potassium hydroxide solution of similar concentration.

The term diazonium salt indicates the resemblance to the ammonium salts in which N is also quinquevalent.

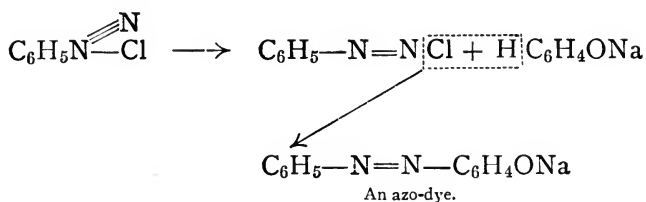
Further decompositions of benzenediazonium halides may be noted.



The diazonium cyanides $\text{R} \cdot \begin{array}{c} \text{N} \\ ||| \\ \text{N—CN} \end{array}$ form colourless compounds whose aqueous solutions resemble a solution of potassium cyanide and possess an alkaline reaction.

The isomeric diazo-cyanides are coloured and possess none of the properties of potassium cyanide.

Another important reaction of diazonium compounds is their conversion into azo-dyes. This takes place in the so-called coupling reactions with amines and the metallic derivatives of phenols.



Too much emphasis cannot be laid on the fact that the preparations described in the foregoing chapter are merely typical examples of general reactions.

CHAPTER XIV

SEPARATIONS EFFECTED BY CHEMICAL REAGENTS

SEPARATION OF AROMATIC HYDROCARBONS FROM HYDROCARBONS OF THE ALIPHATIC SERIES.

Separation of Benzene and "Paraffin Oil."—Measure out 50 c.c. of the mixture (noting the slight blue fluorescence) in a *dry* measuring cylinder. Transfer to a *dry* flask, and add slowly 25 c.c. of fuming (Nordhäusen) sulphuric acid, shaking thoroughly after each addition and cooling well in a *large* vessel of water.

Heat is developed, and the benzene dissolves, forming benzenesulphonic acid (compare page 202). The paraffin oil remains for the most part unacted on, but certain impurities which are present give rise to considerable darkening under the action of the sulphuric acid. The mixture is now slowly poured into about an equal volume of water contained in a litre round-bottomed flask. The flask must be cooled during the addition of the sulphuric acid mixture. The water dissolves both the benzenesulphonic acid and the excess of sulphuric acid; the unchanged paraffin oil remains insoluble.

Two methods for the separation of the paraffin oil can be employed:—

(i) The unchanged oil can be removed by means of a separating funnel, washed with dilute sodium carbonate solution, then with water, and dried over calcium chloride.

(ii) A more convenient method, and more instructive, is that of Steam Distillation, which should be adopted in the present case. The acid mixture in the litre flask, obtained as above, is treated with a thick paste, obtained by rubbing up calcium carbonate in a mortar with water. The addition of this paste is continued till no further evolution of carbon dioxide occurs on adding more. Insoluble calcium sulphate and readily soluble calcium benzenesulphonate are obtained. The mixture is then distilled in steam in the apparatus

indicated in the sketch on page 205; the contents of the distillation flask must be heated almost to boiling before the introduction of the steam. The paraffin oil readily distils over with the steam, while the calcium salts remain behind. The paraffin oil is separated and dried over calcium chloride, after which its volume is noted. It is then distilled, using an air condenser.

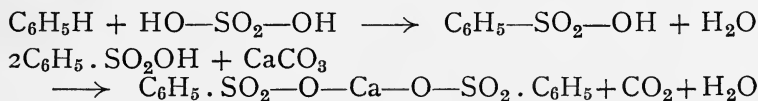
If a light petroleum be present in the original mixture, a water condenser must be used.

The range of temperature over which the paraffin distils should be carefully noted.

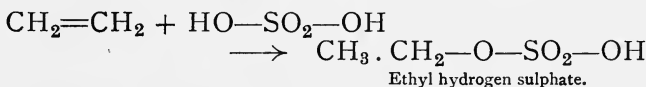
It is desirable to neutralize the excess of sulphuric acid with calcium carbonate or sodium hydroxide, since hot sulphuric acid tends to decompose aromatic sulphonic acids with regeneration of the hydrocarbon. The use of superheated steam facilitates this decomposition.

If the liquor remaining in the distillation flask be filtered from insoluble calcium sulphate by means of a Büchner funnel, calcium benzenesulphonate can be obtained on concentration of the filtrate.

The crystals should be filtered off by means of a pump, and washed with alcohol.



Contrast the action of concentrated sulphuric acid on unsaturated hydrocarbons such as ethylene, in which an ester of sulphuric acid and not a sulphonic acid is produced.



Separation of Hydrocarbons in Complex Mixtures.—For the detection of benzene in complex mixtures of hydrocarbons, the following method may conveniently be employed. The mixture is first distilled, using a fractionating column, and that portion distilling between 78° and 84° , or better 80° and 82° , is collected separately. This is shaken with cold concentrated sulphuric acid till no further darkening in colour occurs. By this means olefines, acetylenes and certain sulphur compounds are removed. Paraffins, naphthenes and aromatic hydrocarbons remain behind. The sulphuric acid layer is then run off, and the residual oil heated with excess

of concentrated sulphuric acid. By this treatment benzene and its homologues are converted into the soluble sulphonic acids.

After cooling, the acid layer is separated from the unchanged paraffins and naphthenes and a current of superheated steam* passed through. In presence of the acid the aromatic sulphonic acids are decomposed, and the regenerated hydrocarbons distil over with the steam.



The oil which distils is separated, washed with dilute caustic soda, then with water, and dried. It is then distilled, using a fractionating column, when that portion distilling between 78° and 84° is collected separately; if the quantity of oil be large, the fraction coming over between 80° and 82° may be collected instead. On cooling in ice, the benzene may be caused to solidify, the portion remaining liquid poured off, and the solid residue tested for benzene by nitration and reduction to aniline (see pages 202-207).

To detect a naphthene hydrocarbon derived from hexamethylene in the portion which is unattacked by fuming sulphuric acid, this mixture is treated with fuming nitric acid, when the naphthene is converted into a nitro derivative of an aromatic hydrocarbon, which is tested for by reduction to an amine and subsequent treatment with sodium nitrite and alkaline β -naphthol. The formation of an azo-dye denotes the presence of a derivative of cyclohexane in the original mixture.

A method for distinguishing between American and Russian petroleum (paraffins and naphthenes of sp. gr. 0.8 to 0.82), which depends on the greater solubility of naphthene hydrocarbons in a mixture of equal volumes of anhydrous chloroform and 93 per cent. alcohol, is described by Riche and Halphen, *Journ. Pharm. Chim.*, 1894, **36**, 289. See also Redwood, "Treatise on Petroleum," ii. 314.

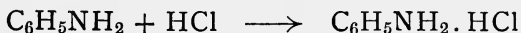
REMOVAL OF THE BASIC CONSTITUENT OF A MIXTURE.

Example: Separation of Toluene and Aniline.

Forty grams of the mixture are placed in a separating funnel and treated with about an equal volume of dilute hydrochloric acid (1 : 3). The mixture is vigorously shaken

* Obtained by passing steam through a heated metal coil.

for two or three minutes (*not less*). The lower layer now consists of an aqueous solution of aniline hydrochloride (phenylammonium chloride, as it might be called).



[Compare the union of ammonia and hydrochloric acid to form ammonium chloride, or "ammonia hydrochloride."]

This lower layer is run off, and the operation repeated with four successive quantities of dilute hydrochloric acid. The four *aqueous* layers containing aniline hydrochloride are, of course, united.

If after separation the fourth hydrochloric acid extraction gives rise to a purple colour when neutralized and treated with excess of a solution of bleaching-powder, this is an indication that all the aniline has not yet been extracted, and treatment with hydrochloric acid should be continued. This test must always be carried out. By this time all aniline should have been removed, and only toluene should remain in the separating funnel. The toluene is now washed once with a little water, the latter run off, and the remaining oil shaken with successive small quantities of (anhydrous) calcium chloride. Any solution of calcium chloride which separates is run off from time to time.

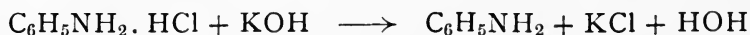
This solution of calcium chloride, however, must not be run into the solution of aniline in hydrochloric acid, otherwise, when the latter solution is rendered alkaline, a precipitate of calcium hydroxide is obtained which renders extraction with ether difficult. The calcium chloride solution should be thrown away.

When no more solution of calcium chloride separates the toluene is allowed to stand for an hour or so over anhydrous calcium chloride in order to remove the last traces of moisture. This method should always be followed when liquids are to be dried; it is usually not sufficient simply to shake with the desiccating agent.

The toluene, which should and *must* be dry, is then poured into a *small*, previously-weighed flask, and its weight determined, whereby the percentage of toluene in the original mixture is found. The toluene so obtained may be purified by distillation, using a water condenser, and collecting only that portion boiling from 109° to 112°. Boiling point of pure toluene 110°.

Treatment of the Aqueous Aniline Hydrochloride Solution.—The acid liquid is rendered alkaline by addition of a *very*

concentrated potassium hydroxide solution. Aniline separates as an oil.



compare—



The mixture is cooled if necessary, placed in a separating funnel, and extracted three times with ether, by vigorously shaking in presence of that solvent.

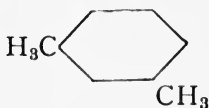
After each extraction, the *lower* aqueous layer is run out, the upper ethereal layer transferred to a flask, the aqueous solution again returned to the funnel, and the extraction repeated.

The ethereal solution of aniline, which will possess a red colour, due to impurities, is dried by shaking with successive small quantities of anhydrous sodium sulphate, or potassium carbonate, and is allowed to remain in contact with the solid for some hours.

The ether is then distilled off, using the apparatus described on page 206. The aniline, B.P. 183° , is then distilled using an air condenser.

REMOVAL OF THE ACIDIC CONSTITUENT OF A MIXTURE.

Example : Separation of *m*-Xylene and Phenol (*m*-Dimethyl benzene and Monohydroxybenzene).



Forty grams of the mixture are shaken in a separating funnel with about an equal volume of caustic soda (sodium hydroxide) solution of about 20 per cent. strength.

A considerable amount of phenol at once dissolves in the alkaline liquid, forming sodium phenoxide.* After shaking up a few times the aqueous lower layer is run off and transferred to a flask and the operation repeated with a fresh quantity of caustic soda, which after shaking several times is



Phenol, however, does *not* dissolve in Na_2CO_3 or K_2CO_3 solution. Xylene is of course, unchanged by aqueous NaOH .

separated as before and mixed with the alkaline liquor previously separated.

N.B.—Especially during the *first* extraction, the contents of the separating funnel must not be shaken too violently, otherwise a slowly separating emulsion may be formed.

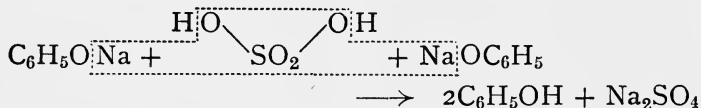
After *three extractions*, wash the remaining xylene by shaking once with water, run the water into the sodium hydroxide extract, add more water, shake, run off and add about 2 c.c. of ferric chloride solution to the *last* separated water. If no purple colour appears, all phenol has been removed; if such a colour be produced, the mixture must be submitted to further extraction with sodium hydroxide solution.

One washing of the xylene with water before testing with FeCl_3 is necessary to remove sodium hydroxide which would otherwise cause the precipitation of gelatinous ferric hydroxide $\text{Fe}(\text{OH})_3$ *i.e.* $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, thus preventing the production of the purple colour.

The xylene layer which *must* be free from phenol is separated from the water and shaken up with successive *small* quantities of anhydrous calcium chloride, after which it is allowed to remain in contact with the latter for an hour, transferred to a DRY, weighed flask, and its weight determined.

It may be purified by distillation, using a small flame, and an AIR condenser. The fraction boiling from 138° to 140° may be considered pure. (Boiling point of *m*-xylene is 139° .)

Separation of Phenol from the Alkaline Extract.—The alkaline extract consists of an aqueous solution of sodium phenoxide $\text{C}_6\text{H}_5\text{—O—Na}$ mixed with excess of sodium hydroxide. It is rendered *permanently* acid with dilute sulphuric acid (1:2) and *well stirred*. This neutralizes the excess of sodium hydroxide and liberates phenol.



The strongly smelling liquid is now transferred to a separating funnel and extracted at least three times with ether, as described under aniline, page 215.

N.B.—The ether-phenol solution forms the UPPER LAYER.

The solution of phenol in ether is now dried over pieces of fused ANHYDROUS sodium sulphate, the ether distilled off (as described on page 206) in a weighed distilling flask

containing a small piece of porous tile weighed WITH the flask.


The residual phenol, freed from ether + the distilling flask + the porous tile is then weighed. It can be purified by distillation, using an AIR condenser.

The phenol may also be estimated by acidifying its alkaline solution in a flask provided with a long graduated neck, the phenol rises to the surface, and its volume is measured.

CHAPTER XV

THE DESTRUCTIVE DISTILLATION OF COAL

It was noted by several experimenters at the beginning of the eighteenth century that inflammable gases were evolved when coal was heated, but the first suggestion that the gas should be manufactured on the large scale and conveyed in pipes was made by Murdoch in 1792 as a result of experiments carried out by him in Redruth, Cornwall. Space, however, entirely forbids a historical account of the development of the illuminating gas industry up to the position which it occupies to-day. We must, therefore, at once deal with the essential details of the plant employed in gas manufacture and with the more important bye-products which are produced.

The heating of the coal is carried out in retorts constructed of very refractory firebrick. There are at present three distinct shapes of gas-retorts in use, namely: (i) the horizontal -shaped retort about 20 feet long; (ii) the inclined retort of a similar shape about 15 feet long; (iii) the tapering vertical retort.

In the early days of gas manufacture and indeed until comparatively recently, the retorts were heated by means of coke fires. The method almost universally adopted at the present time, however, is to use producer gas which is allowed to burn in chambers built round the retorts, whereby regular heating and a very high temperature are secured. The producer gas is obtained by passing air through a mass of red-hot coke. An enormous saving in the last-named substance has resulted from the use of this gaseous fuel.

The older horizontal retorts, which are usually provided with gas-tight doors at each end, were, and in many cases are still, charged and emptied by means of shovels and rakes worked by several men. Certain mechanical methods have, however, been adopted recently. The gas escapes through vertical pipes.

The inclined retorts, having an angle of slope of about

30° to 36°, are charged at the upper end by means of a hopper. On opening the lower door most of the coke falls out without the use of rakes. These retorts, which have greatly diminished the manual labour required for gas production, have only recently been introduced.

In the earliest days of gas manufacture, *i.e.* from about 1800 to 1860, it was essential that the gas supplied should possess a high natural luminosity, *i.e.* when burnt from a batwing burner the flame should be as luminous as possible.

Now, it was soon discovered that the lower the temperature at which the coal was distilled the greater luminosity did the gas possess. On the other hand, if the temperature were higher and the heating more prolonged a much larger volume of gas was obtained. The high luminosity of the gas produced at a lower temperature is due to the presence of considerable quantities of the so-called heavy hydrocarbons such as ethane C_2H_6 , ethylene C_2H_4 and benzene C_6H_6 , whilst with increase in the temperature at which the coal is "carbonized" or "de-gassed," the gases evolved become richer in methane and at a still higher temperature hydrogen predominates. The instability of ethane and ethylene at high temperatures is well known.

The largely increased volume of gas obtained at a higher temperature is due therefore to a more complete degradation of the gaseous and tarry products resulting from the distillation.

Since the introduction of the Welsbach and other incandescent mantles it has not been so necessary to produce gas possessing a high natural luminosity, since practically the whole of the light emanating from an incandescent mantle is due to the glowing of the oxides of which it is composed; the gas itself is largely diluted with air so that the conditions are those which exist in the non-luminous flame of a Bunsen burner.

In consequence, the authorities of the gas works have turned all their attention to obtaining the maximum yield of gas from a given weight of coal in so far as this is compatible with maintaining a satisfactory quality of the tar and coke which are simultaneously produced.

Since incandescent mantles are, however, by no means universally used and since the calorific power of the gas must not unduly be diminished, it is customary to enrich it by the addition of about 10–20 per cent. of carburetted water gas. This is obtained by passing steam over coke maintained at a red heat. The mixture of hydrogen and carbon monoxide so produced possesses no luminosity and is passed through a

chamber heated to redness, and into which high-boiling petroleum is injected. This is immediately "cracked," giving rise to volatile products which pass on with the water gas ($\text{CO} + \text{H}_2$) into another chamber known as a superheater, where the decomposition into non-condensable gas of any oil which has been carried forward mechanically is effected. The resulting gaseous mixture burns with a very luminous flame, and is known as "carburetted water gas."

It has been found that not only is the illuminating power of the gas dependent on the temperature at which carbonization takes place, but also to a certain extent on the quantity of coal placed in the retorts.

If the retorts are only about one-third full considerable decomposition of the gaseous hydrocarbons takes place long before they leave the retort. This is due to the heat radiated from the sides of the retort.

Thus the ethylene is decomposed yielding carbon, methane and other hydrocarbons, while benzene will be partly converted into diphenyl, a more complex and less volatile hydrocarbon. A further portion of the benzene will break up yielding acetylene, which as has recently been shown, is capable under the influence of heat of condensing to form a whole series of complex hydrocarbons of high boiling point.

In consequence of these decompositions undergone by the so-called heavy hydrocarbons, the luminosity of the gas is diminished.

If, on the other hand, the charge of coal be sufficient almost entirely to fill the retort, the evolved gases must perforce leave the retort sooner. Moreover, practically the whole of the sides of the retort are in contact with the coal or the coke produced therefrom and not with the gas, so that the undesirable radiation effect referred to above is largely eliminated.

It is, moreover, obvious that a considerable amount of labour is saved by introducing large charges into the retorts, since it will not be necessary to empty them so often; wear and tear of the charging machinery (where this is employed) is also diminished.

We have discussed the advantages of the completely filled horizontal or inclined retort: we shall now see that vertical retorts are even more satisfactory provided they be always kept full.

The coal is introduced into the top of the retort, while coke is withdrawn at the bottom. To facilitate the passage

downward of the charge, the internal cross-section of the retorts is larger at the bottom than at the top.

Owing to the fact that a layer of non-conducting coke is formed close to the sides of the retort, the interior of the charge remains comparatively cool, and consequently the ethylene, ethane and benzene suffer little decomposition as they pass upwards.

The tar obtained from vertical retorts contains less free carbon than that from the older kinds: when we remember that in the decomposition of ethylene, ethane, etc., carbon is liberated, the reason for this difference is at once apparent.

Hydrocarbons, however, are not the only gases which suffer decomposition through radiation from the hot sides of the older types of retort. Ammonia is an important constituent of the gases evolved in the distillation of coal, but it is unstable at high temperatures, decomposing into nitrogen and hydrogen. It is found that the yield of ammonia from vertical retorts is 50 per cent. greater than from horizontal. (On the other hand, less cyanogen is produced.) If the removal of the ammonia from the retort be accelerated by the introduction of a stream of inert gas, the percentage in the coal gas is increased, since more ammonia escapes thermal decomposition (see under Shale distillation). If steam be introduced into the retort a further increase in the yield of ammonia is observed, and the percentage of nitrogen in the residual coke is found to be diminished.

The increased ammonia production is accompanied by a falling off in the amount of cyanogen produced. This is in agreement with the observed fact that the maximum yield of cyanogen is always obtained from the most strongly heated retorts containing only small charges of coal.

The conditions, therefore, which favour the production of ammonia militate against that of cyanogen. It may be that the formation of cyanogen requires the presence of free nitrogen, resulting from the dissociation of NH_3 under the influence of higher temperatures.

For an account of the various methods in vogue, and the plant employed for the purification of coal gas, the reader is referred to some of the numerous and exhaustive treatises dealing with the subject.

The following results obtained on the distillation of various samples of coal at successive temperatures initially of 400°C ., then 600° , 850° , 1000° , and finally 1200° , may be interesting in this connexion. Each of these temperatures was

maintained until the evolution of gas had almost ceased, after which the temperature was raised to the next higher stage. The experiments are described by Vignon (*Compt. rend.*, 1912, 155, 1514, and *Journal of the Chemical Society*, 1913, *Abstracts*, section I. page 153).

The results show (1) that the unsaturated hydrocarbons, such as acetylene, ethylene, etc., almost all pass over below 600° and disappear entirely at higher temperatures; (2) methane and its homologues are very abundant (forming 60–80 per cent. of the total gas) up to 800°, after which they decrease rapidly with the rise in temperature; (3) from 800° to 1000° hydrogen predominates, but this in its turn diminishes above 1000°; (4) very high temperatures favour the formation of carbon monoxide.

Vignon also finds that a rise in the temperature of distillation produces an increase in the total volume of gas evolved, but a diminution in its calorific power.

Bye-product Recovery Coke-ovens.—So far we have only considered those processes in which coal is distilled with the primary object of yielding gas. Owing to the fact that the coke obtained at the gas works (with the possible exception of that prepared in the new vertical retorts) is too light and porous for use in metallurgical operations, a large amount of coal is distilled or “de-gassed” in specially constructed ovens with the object of preparing the so-called metallurgical coke. Most of these “bye-product recovery coke-ovens” are worked in Germany, and the method adopted consists in carrying out the distillation of the coal at as high a temperature as possible. The gases are drawn off and the tar and ammoniacal liquor separated by suitable methods. After this the gases are not used for illuminating purposes (owing to the high temperature of their production their luminosity would be very low), but are led back and used for heating the coke furnaces.

It may be mentioned that the required compactness of the coke is secured by charging the ovens with high piles of coal so that the lower layers are pressed down by those above.

The working up of the tar and ammonia produced in these coke-ovens is a very important branch of the industry.

The tar from coke-ovens and also from vertical gas retorts contains less free carbon and less pitch than that obtained by the older methods of carbonization. It is therefore of a thinner consistency.

Distillation of Coal in a Vacuum.—Although low pressures have not yet been employed in the distillation of coal on a manufacturing scale, it is worthy of note that various experiments have recently been made by chemists with the object of determining to what extent the nature of the products obtained depends on the pressure at which the distillation is carried out.

The experiments of Pictet and Bouvier (*Berichte der deutschen Chemischen Gesellschaft*, 1913, **46**, 3342; *Journal of the Chemical Society, Abstracts*, 1913, section I., page 1315) were made with a bituminous coal from Montrambert (Loire), France, which, when distilled under ordinary conditions, yielded 15–18 per cent. of gas and 15–20 per cent. of condensable products.

Thirty kilograms of this coal, in quantities of 2–5 kilograms at a time, were heated in a vertical iron retort of about 10 litres capacity; the temperature was slowly raised to 450° Centigrade, and a pressure of a few centimetres of mercury maintained by means of water pumps. Each experiment usually occupied about five hours.

Of the products of distillation only the tar has been carefully investigated; it is unfortunate that a thorough examination of the gas was not made, the authors state that this resembled butadiene (I) and isoprene (II) in odour.



The water which distilled was found to have an acid reaction, and to be free from ammonium salts. This is one of the most remarkable results of the whole investigation.

The coke was found to yield further quantities of combustible gas when heated more strongly.

The tar produced was of a clear brown colour, and resembled petroleum in odour. It was lighter than water, and amounted to about 4 per cent. of the weight of the coal. This tar, it is most interesting to note, contained no phenols, but was very rich in nitrogenous bases, especially those of the secondary type.

After removal of these bases, careful fractionation of the residual liquid under reduced pressure failed to indicate the presence of any solid substances, *e.g.* paraffin wax, and oxidation of the various fractions yielded only aliphatic acids, thereby indicating the absence of aromatic hydrocarbons.

The action of sodium on certain fractions of the vacuum tar removed certain hydroxy compounds which, after regeneration from their sodium derivatives by means of water, exhibited the usual behaviour of alcohols towards acetyl chloride or benzoyl chloride, pleasant-smelling esters being produced.

The hydrocarbon residues remaining after the treatment with sodium were found to contain considerable amounts of unsaturated hydrocarbons, and also two naphthenes $C_{10}H_{20}$ and $C_{11}H_{22}$. For the views held by Pictet and Bouvier concerning the constitution of these substituted polymethylenes, the original paper should be consulted.

The light brown vacuum tar was then decomposed by distilling it at the ordinary pressure through a red-hot iron tube packed with coke with the object of imitating as closely as possible the actual conditions which obtain in a gas retort.

A considerable quantity of gas, resembling coal gas in odour, was produced, which consisted mainly of hydrogen and paraffin hydrocarbons.

An aqueous distillate containing much ammonia was obtained and a dark coloured tar resembling ordinary coal tar in odour.

This tar, unlike the original product, contained phenols, bases recalling the odour of pyridine, and aromatic hydrocarbons, amongst which benzene, naphthalene and anthracene could be identified.

Pictet and Bouvier tentatively suggest that in the process of coal distillation as carried out at the gas works, the methane, ammonia, phenols, and aromatic hydrocarbons are not primary products, but are formed by the decomposition of intermediate, more complex substances represented by the above "vacuum tar." (Compare, however, the results of Jones and Wheeler, page 225.) It should, however, be noted that the absence of methane from the gaseous products of distillation was not proved (see above), while Burgess and Wheeler obtained this gas in experiments very similar to those just described.

Further experiments on the subject are therefore very necessary.

Burgess, Jones, and Wheeler* have also carried out some important experiments on the products, both gaseous and liquid, which are obtained when various bituminous coals are distilled in vacuo.

* Burgess and Wheeler, *Trans. Chem. Soc.*, 1914, 131; Jones and Wheeler, *ibid.*, 140.

By gradually heating coal contained in an apparatus evacuated by means of a Sprengel pump, the gases evolved at various temperatures up to 450°C . were collected and analysed. For a detailed account of their experiments the reader should consult the original papers. The gases were found to contain hydrogen sulphide, the oxides of carbon, ethylene and the higher olefines, hydrogen, and the paraffin hydrocarbons from methane to pentane.

The following extract from the paper by Jones and Wheeler will serve to indicate the nature of the products obtained.

"Propane and butane mostly appear at the lower temperatures of distillation, the range 100° – 300° being attended by the greatest percentage evolution; above 350° the percentage of methane increases and that of the higher hydrocarbons decreases."

"Bituminous coals when distilled in a vacuum (5 to 40 mm.) at temperatures up to 430° , yielded, besides gaseous products and water, about 6.5 per cent. of their weight of tar. On distilling this tar, about half remained as pitch, boiling above 300° . The oils boiling below 300° contained the following substances.

(i) Unsaturated (ethylenic) hydrocarbons of indeterminate composition, for the most part richer in carbon than the mono-olefines C_nH_{2n} . These formed between 40 and 45 per cent. of the oils.

(ii) Naphthenes (C_nH_{2n}) and liquid paraffins, the former greatly predominating, forming together about 40 per cent. of the oils.

(iii) Phenols, chiefly cresols and xylenols (between 12 and 15 per cent.).

(iv) Aromatic compounds (about 7 per cent.) apparently homologues of naphthalene, although naphthalene itself did not appear to be present.

(v) A solid paraffin in small quantity, of which the molecular weight was 373.7, that is, intermediate between the values required for $\text{C}_{26}\text{H}_{54}$ and $\text{C}_{27}\text{H}_{56}$.

(vi) Pyridine bases in very small quantity.

"Benzene, anthracene, and carbon disulphide were absent, nor was there any evidence of the presence of toluene or other homologues of benzene in more than minute quantity.

"The water distilled from the coal contained hydrochloric acid and traces of ammonium chloride."

From a comparison of the results of Wheeler and his co-workers with those obtained by Pictet, it will be seen that

in both cases considerable amounts of unsaturated hydrocarbons and naphthenes were obtained. The aqueous distillate was in both cases acid, though Pictet did not observe the traces of ammonia reported by the English chemists.

On the other hand, Wheeler found solid paraffins, phenols and homologues of naphthalene, which were absent in the "vacuum tar" of Pictet.

Possibly the discrepancies are due to differences in the nature of the coals employed, and also to the fact that Wheeler's distillations occupied several weeks, Pictet's only as many hours.

The important bearing which these results have upon the question of the chemical nature of coal is discussed at some length by both the English and foreign chemists.

It would also appear from a closer consideration of Jones and Wheeler's paper that further work with a view to determining the possible yield of low-boiling hydrocarbons under different conditions, with a view to their utilization for internal combustion engines, would be welcomed by many. On pages 146-147 of their paper we read, "Oils of very low boiling point were removed from the gases collected, by passing the latter slowly through a condenser cooled by solid carbon dioxide and ether. The liquid so obtained . . . was found to boil between 35° and 125° ."

CHAPTER XVI

THE DISTILLATION OF COAL TAR

AS we have seen in the last chapter, there are four chief crude products obtained by the destructive distillation of coal, namely, gas, tar, ammoniacal liquor and coke.

Enough has been said already to indicate the great extent to which the yields of these various products are dependent on the temperatures employed in the distillation and also on the shape of the retorts and the amount of free space remaining therein. It is perhaps unnecessary to add that another important, perhaps *the* most important, determining factor is the nature of the coal which is distilled.

When the vapours evolved from the gas retorts or from the coke-ovens are passed through the so-called hydraulic mains, condensers or scrubbers, the condensed products separate into two layers, the upper one consisting of an aqueous solution of ammonia and ammonium sulphide known as ammoniacal liquor, while the heavier lower one is a thick black liquid possessing a powerful odour, different, however, from that of the upper aqueous layer. This is known as coal tar.

On standing, the ammoniacal liquor rises to the surface, is mechanically separated and is then treated in a suitable vessel with excess of a hot aqueous suspension of calcium hydroxide (milk of lime). On heating, the liberated ammonia is passed directly into sulphuric acid with the formation of ammonium sulphate, which finds considerable application as an artificial manure.

The tarry liquor which is immiscible with the water, is a very complex mixture. Its black colour is due to suspended particles of carbon, but its peculiar odour can hardly be ascribed to any one constituent. Its specific gravity is about 1.1 to 1.2.

Crude undistilled tar is employed to a certain extent in the preservation of wood and brickwork, and in the manufacture of waterproof felt for the roofs of outhouses.

The tar, after being freed as completely as possible from water, is introduced into large iron retorts, capable of holding several tons. These are frequently heated simultaneously on

the outside by a fire, and inside by means of pipes fed with superheated steam.

A certain amount of water and ammonia passes over with the first distillate, and during their elimination the liquid in the retorts tends to froth, splutter, and bump. Simultaneously, however, a light yellow oil distils, the specific gravity of which increases as the temperature of distillation rises till the portion distilling above 170° is slightly heavier than water.

In most tar distilleries four principal fractions are collected:—

	Boiling point.
Light oil	80° – 170°
Middle oil (or carbolic oil)	170° – 230°
Heavy oil (or creosote oil)	230° – 270°
Green oil (or anthracene oil)	above 270°

When the temperature reaches 270° , and the anthracene oil begins to come over, the distillation is continued under diminished pressure, whereby much of the decomposition which would otherwise occur is prevented. In order to prevent the pitch remaining in the still from setting hard and turning to coke, a current of steam is introduced at the same time. In some cases where the tar contains large quantities of free carbon, steam is introduced at a temperature as low as 170° C.

We may now consider in some detail the constituents of these fractions, and the uses to which they are put.

LIGHT OIL.

This, on repeated fractionation, yields principally benzene C_6H_6 , toluene $C_6H_5 \cdot CH_3$, and the three isomeric xylenes $C_6H_4(CH_3)_2$.

Note.—The “first runnings” obtained on redistillation of the “light oil” come over before the C_6H_6 , and contain carbon disulphide CS_2 , pentane C_5H_{12} , hexane C_6H_{14} and acetonitrile $CH_3CO \cdot CN$, all of which substances have extremely low boiling points.

Benzene and toluene can be separated from each other and from the xylenes owing to the difference in their boiling points, but it will be readily seen that such a method is impossible of application for the separation of ortho-, meta- and para- xylenes. In order to effect such a separation, the crude “xylene” is treated at the ordinary temperature with sulphuric acid. The ortho- and the meta- compounds form sulphonic acids, $C_6H_3(CH_3)_2SO_2 \cdot OH$, which dissolve. The

p-compound is not sulphonated under these conditions, and remains behind.

The mixed sulphonic acids are then converted into their sodium salts, which are separated by repeated fractional crystallization, the sodium salt of the ortho- acid being the more sparingly soluble. From each of the pure salts the corresponding hydrocarbons can be regenerated by addition of excess of sulphuric acid, and treating with superheated steam.

Compare Chapter XIV., page 212.

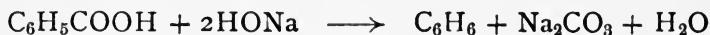
Other aromatic hydrocarbons occurring to a lesser extent in the light oil are also indicated below :

	Boiling point.
Benzene	80.4°
Toluene	110°
Ortho-xylene $C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$	142°
meta-xylene	139°
para-xylene	138°
Mesitylene $C_6H_3 \begin{matrix} \diagup CH_3 \text{ 1} \\ \text{---} CH_3 \text{ 3} \\ \diagdown CH_3 \text{ 5} \end{matrix}$	165°
Pseudocumene $C_6H_3(CH_3)_3$ 1.3.4	169.8°

Benzene C_6H_6 .—This hydrocarbon is also obtained when acetylene gas is passed through a red-hot tube—



and also when benzoic acid, which occurs naturally in "Gum Benzoin," is heated with soda lime—



Benzene is frequently known as benzol, the word being borrowed from the German. Its use by English chemists is, however, wholly inadmissible, since the termination -ol denotes an alcohol or a phenol. See, however, page 230.

Benzene, which is a pure hydrocarbon of the aromatic series of perfectly definite composition, must not be confounded with the ill-defined mixture of aliphatic hydrocarbons usually known as Benzine. Occasionally liquids sold as benzine may contain some benzene, C_6H_6 , but the name is usually given to the low-boiling fractions obtained during the fractionation of American petroleum, and which consist of pentane C_5H_{12} , hexane C_6H_{14} and heptane C_7H_{16} .

For most commercial purposes benzene need not be perfectly free from other aromatic hydrocarbons, indeed, their presence is frequently an advantage, since the freezing point of benzene is thereby considerably depressed.

The "90 per cent. benzol" employed as a motor spirit is crude benzene, 90 per cent. of which distils below $100^{\circ}\text{C}.$, the remainder up to about 140° . It contains 70–75 per cent. benzene, 22–24 per cent. toluene, traces of xylenes and other hydrocarbons and carbon disulphide.

The "50 per cent. benzol," *i.e.* a mixture of aromatic hydrocarbons, of which 50 per cent. distils below $100^{\circ}\text{C}.$, contains approximately 50 per cent. benzene, 35–40 per cent. toluene and approximately 10 per cent. of xylenes.

The term "benzol," therefore, if used at all by English chemists, should be clearly understood to be only a trade name for various mixtures containing, in addition to benzene, certain higher homologues such as toluene and xylene.

Solvent Naphtha, which is used as a rubber solvent in the manufacture of waterproofed cloth, distils between 120° – $160^{\circ}\text{C}.$, and contains toluene, xylene, and pseudocumene.

Enormous quantities of benzene are converted into nitrobenzene and thence to aniline, which finds wide application in the dye industry. For preparation and properties of these two substances, see pages 202–207, and for further chemical properties of benzene, see under "Preparation of Benzene," page 201.

Toluene, Monomethylbenzene $\text{C}_6\text{H}_5\text{—CH}_3$ is a colourless hydrocarbon, B.P. 110° , which can also be obtained by heating Balsam of Tolu, whence its name.

Its formation from this resin depends on the elimination of carbon dioxide from the toluic acid which it contains—

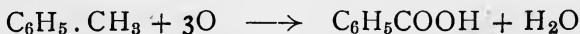


It is also obtained by the action of sodium on a mixture of methyl iodide and iodobenzene.



Some of its uses have been described under "Benzene." It is the starting-point in the preparation of saccharin, the well-known sugar substitute.

Its effect in producing increased fertility of the soil in laboratory experiments has recently created much interest. With potassium permanganate, or nitric acid (dilute), toluene gives benzoic acid.



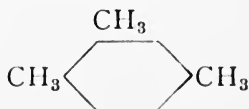
Xylenes.—Coal tar xylene contains about—

70–87 per cent. *m*-xylene.
 2–15 „ „ *o*-xylene.
 3–10 „ „ *p*-xylene.

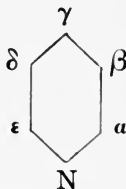
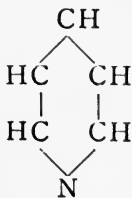
The separation of the three isomers is described on page 228.

Mesitylene, Symmetrical Trimethylbenzene, is of theoretical interest, since its formation from acetone under the condensing influence of sulphuric acid is a good example of the transformation of an aliphatic to an aromatic compound.

Pseudocumene.—This hydrocarbon has the constitution—



Basic Constituents of the Light Oils.—In addition to a certain amount of ammonia derived from incompletely separated “ammoniacal liquor,” the light oils contain pyridine C_5H_5N , and certain of its methyl derivatives. These substances possess basic properties, and are removed from the light oils by shaking out with sulphuric acid. After separating the undissolved oil the basic substances can be obtained by addition of excess of alkali to the solution of their sulphates. (Compare the practical exercise on page 214.) The method adopted in practice, however, is to saturate the solution with ammonia gas, when pyridine and its homologues separate as an oil. Pyridine has the formula—



There are *three* methyl pyridines, or picolines, as they are called, since the methyl group may replace a hydrogen atom attached to one of the carbon atoms α , β or γ . Carbon atoms ϵ and δ are obviously equivalent to α and β . Six different picolines cannot therefore exist, but only three. Pyridine and many of its homologues are also obtained from

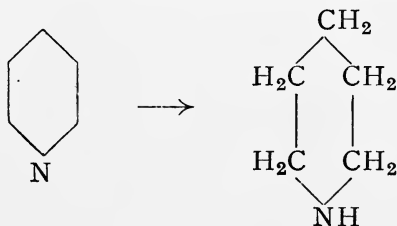
Dippel's oil, an unspeakably evil-smelling liquid obtained by the dry distillation of bones which still contain fatty matter.

It should be noted that the nitrogen atom forms part of the ring. In writing the formula the hydrogen atoms are frequently omitted as in the case of the benzene ring.

Pyridine is a colourless liquid, B.P. 114° . It possesses an odour resembling that of a foul tobacco pipe. With water it is miscible in all proportions.

Boiling nitric or chromic acids do not attack it. Sulphuric acid forms a sulphonic acid at about 300° . It is, therefore, a much more stable substance than benzene.

On boiling with sodium and ethyl alcohol, or by electrolytic reduction, pyridine takes up six hydrogen atoms forming piperidine, which has an odour resembling that of pepper.



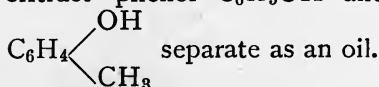
The alkaloid nicotine obtained from tobacco is a derivative of pyridine, while piperine, a basic substance occurring in black peppercorns, is derived from piperidine.

In Germany pyridine is used for denaturing alcohol for industrial purposes.

MIDDLE OR CARBOLIC OIL.

When the fraction distilling between 170° and 230° is allowed to stand, or better still, when it is cooled in ice, crystals of naphthalene are deposited. These are separated by centrifugalizing and pressing. Impurities are removed by addition of concentrated sulphuric acid, which converts them into sulphonic acids, and the naphthalene is purified by sublimation and recrystallized in special vessels from low-boiling petroleum.

After removal of the naphthalene the remaining oil is fractionally extracted by shaking with 10 per cent. sodium hydroxide solution. On acidification of the separated alkaline extract phenol C_6H_5OH and the three isomeric cresols

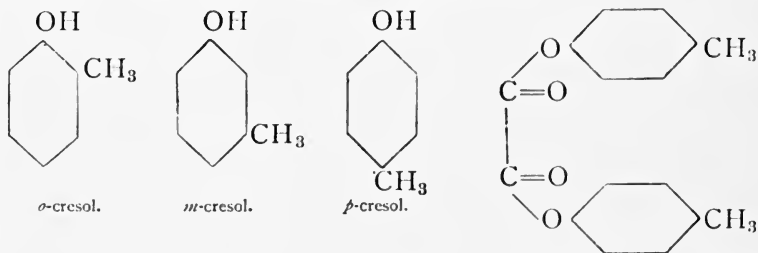


The phenol is obtained pure by fractional distillation.

The German Patents 137584 and 141421 give information dealing with the separation of the three cresols. The commercial cresol contains *o*-, *m*- and *p*-cresols. The ortho-cresol is removed by fractional distillation, since it boils at 188° , while *m*- and *p*-cresols boil at 201° and 198° respectively.

The two remaining isomers are heated with anhydrous oxalic acid or with anhydrous potassium hydrogen oxalate. By this means the *p*-cresol ester of oxalic acid is produced and can be separated in crystals, which are soluble in alcohol or ether, but not in benzene. The *m*-cresol does not react with the oxalic acid or oxalate and remains unchanged. After the *p*-cresol ester of oxalic acid has been purified by sublimation it is treated with water which liberates pure *p*-cresol and oxalic acid, which is thereby recovered.

The formulæ of the three cresols and of the di-*p*-cresol ester of oxalic acid are indicated below—



The di-*p*-cresol ester of oxalic acid.

Naphthalene.— $C_{10}H_8$ is a white crystalline hydrocarbon possessing a characteristic odour. It melts at 80° , boils at 218° C., and readily volatilizes at ordinary temperature. Its synthesis has been effected in several ways, but a description of the methods employed would fall outside the scope of this book. The whole of the naphthalene of commerce is obtained from tar.

Naphthalene is, moreover, always present to a certain extent in coal gas, and in cold weather is deposited in the mains, thus occasionally causing obstructions.

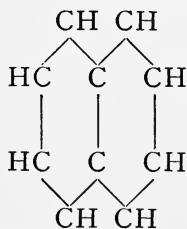
This aromatic hydrocarbon is carefully to be distinguished from the various mixtures of liquid hydrocarbons loosely designated as "naphtha," in which it does not occur.

Formula of Naphthalene.—Since naphthalene is a saturated hydrocarbon of which the chemical properties in many instances resemble those of benzene, a similar structural formula has been assigned to it. It must not be forgotten, however, that

this formula, which is indicated below, does not satisfactorily explain all the known properties of the substance (compare Chapter I., page 45).

As in the case of benzene, the question of the fourth valency of each carbon atom is left out of consideration, and for convenience the hydrogen atoms are usually omitted.

Naphthalene is the first compound we have so far met with, which contains what are known as condensed benzene rings.



usually written

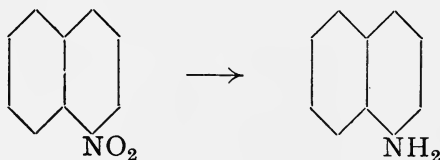


The same method of writing the formulæ of substitution products of naphthalene is employed as in the case of benzene.

Nitro-, bromo-, chloro-, amino- and hydroxy-, as well as alkyl substitution products of naphthalene are well known.

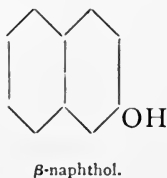
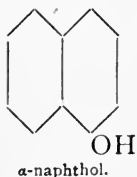
Naphthalene can also readily be sulphonated, and certain of its substituted sulphonic acids are used in the manufacture of dyes.

The nitro derivatives of naphthalene also find considerable application in the manufacture of dye-stuffs, since they can readily be reduced to the corresponding primary amine from which dyes may be obtained.



The hydroxynaphthalenes are known as naphthols, and occur in coal tar. They can be prepared from the naphthalene sulphonic acids by fusing with alkalis (compare preparation of phenol, page 52).

In the case of naphthalene two isomeric mono substitution derivatives are found to exist, in one of which the substituent is attached to a carbon atom adjacent to the second nucleus, denoted the α -derivative, whilst in the β -derivative the substituent is attached to a carbon atom which is not in this position.



When heated with concentrated sulphuric acid in presence of mercuric sulphate one of the benzene nuclei of naphthalene is oxidized, and an *o*-dicarboxylic acid of benzene, known as phthalic acid, is produced.

During the last few years enormous quantities of naphthalene have been used as the starting-point for the preparation of synthetic indigo.

It is also employed for preserving clothes from insect pests, a use which has frequently given rise to an unfortunate confusion with the very different substance camphor; for this purpose it is generally sold under the name of "carbon."

CREOSOTE OIL.

This is the fraction of B.P. 230° – 270° obtained in the distillation of crude coal tar, of which it forms about 10 per cent. It is also known as "heavy oil," and is a very complex mixture of hydrocarbons and phenolic substances, containing among other substances naphthalene $C_{10}H_8$, methylnaphthalene $C_{10}H_7 \cdot CH_3$, certain hydrocarbons of the paraffin series, cresols (monohydroxytoluenes), xyenols (monohydroxyxylenes) and naphthols (monohydroxynaphthalenes).

The separation of the various substances contained in the oil is not carried out to any considerable extent, but the crude oil finds many applications. The most important is in the preservation of timber, such as railway sleepers and telegraph poles, which are treated in large cylinders with the warm oil under pressure for several hours.

Creosote oil is also used as a fuel, and in the manufacture of lamp black and disinfectants, such as Lysol.

The efficiency of these disinfectants is due to the cresols they contain. They are prepared by boiling creosote oil with potash lye (*i.e.* a crude aqueous potassium hydroxide solution) and fats. The soap which is produced forms an emulsion with the creosote oil, which does not separate even on dilution with water. In the absence of soap creosote oil is practically immiscible with water.

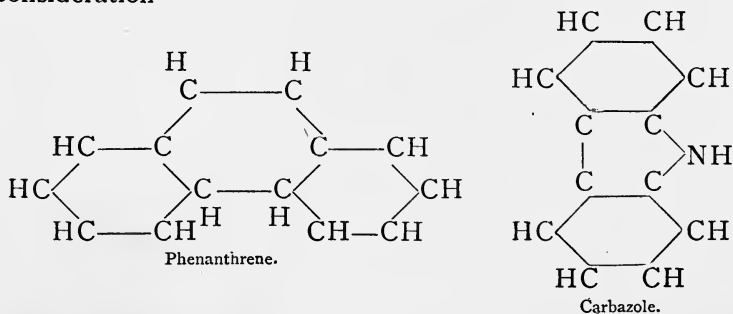
"Creoline" is another disinfectant obtained from creosote oil (of which it may contain as much as 20 per cent.) by boiling with rosin soap.

ANTHRACENE OIL OR GREEN OIL.

The heavy reddish liquid possessing a green fluorescence which distils over above 270° consists principally of anthracene $C_{14}H_{10}$ and phenanthrene $C_{14}H_{10}$ along with some carbazole $C_{12}H_9N$.* These substances separate in crystals on cooling. The oil is redistilled, and by centrifugalizing and submitting the crystals to a high pressure, whereby impurities are squeezed out, a product is obtained which is known as "50 per cent. anthracene." By distilling this with potassium carbonate, carbazole and certain other impurities are converted into potassium derivatives, *e.g.* from carbazole $C_{12}H_8NK$ is produced. Anthracene and phenanthrene distil over unchanged, and the phenanthrene is removed from the solid mixture by extraction with carbon disulphide. The remaining anthracene is purified by crystallization from benzene. It forms colourless plates with a bluish fluorescence, M.P. 213° .

The purification of 50 per cent. anthracene may also be effected by washing with solvent naphtha (see page 230) containing pyridine bases, which more readily dissolves out the carbazole than do the toluene and xylene of the solvent naphtha alone.

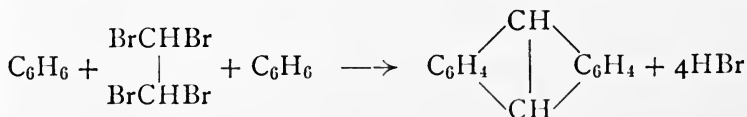
Phenanthrene and carbazole possess relatively little commercial importance. Their constitutional formulæ and that of anthracene are indicated below, the question of the fourth valency of each carbon atom being left out of consideration—



* In addition, naphthalene, diphenyl, methylanthracene, and pyrene are present. For a description of all but naphthalene a larger text-book should be consulted.

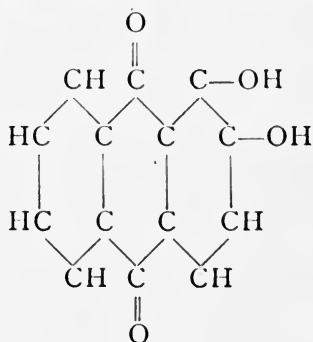
It is interesting to note that the well-known alkaloid morphine (the term "Morphia" is contrary to present-day systems of nomenclature) is probably a complex derivative of phenanthrene.

Anthracene may be synthesized by the action of tetrabromoethane on benzene in presence of aluminium chloride.



Large quantities of anthracene, obtained exclusively from coal tar, are employed in the synthetic production of alizarin, the well-known colouring matter to which the properties of madder root are due.

Alizarin has the formula—



For the estimation of anthracene in commercial 40 per cent. or 90 per cent. anthracene, see "Industrial Chemistry, Organic," Martin (Crosby Lockwood and Son, 1913), page 421.

DISTILLATION OF COAL TAR. PRACTICAL DETAILS.

Before the tar coming direct from the gas-works can conveniently be distilled it should be allowed to stand for some days in a cylindrical vessel fitted with a tap at the bottom. By this means a considerable amount of ammoniacal liquor which, even after the preliminary separation at the gas-works, still remains mixed with the tar, rises to the top and the tar can be run off below. The separation is, however, not perfect.

About 500 c.c. to one litre of the separated tar is then placed in a large round-bottomed glass or copper flask of about $1\frac{1}{2}$ to 2 litres capacity. This is fitted with a broad delivery tube, bent at an acute angle and leading to a water condenser. The bend of the delivery tube should be quite close to the cork, otherwise at a later stage of the distillation it will be found to cool the vapour too much, thereby causing it to condense and run back into the distillation flask, consequently retarding distillation. The water condenser should be connected by means of an adapter and cork with a filter flask which, as in the distillation of ether, is provided with a rubber tube to carry away uncondensed inflammable vapours.

The flask, which should be placed over a large iron tray, is then gently and cautiously heated by means of a free flame which is kept in constant motion.

Distillation soon commences, and as the temperature rises towards 100°C ., it is liable to be accompanied by frothing and sudden evolution of steam, owing to the dropping back of condensed steam into the hot contents of the flask, and to the superheating of globules of water suspended in the tar. The temperature indicated by the thermometer should not be allowed to rise far above 100° before the "bumping" has ceased; otherwise the danger of the formation of superheated steam will be increased since, obviously, the temperature of the heated tar must already be considerably greater than 100° .

A pale yellow oil mixed with much water and ammonia distils over. After 100° is registered the distillation proceeds more steadily owing to the complete removal of the water. The water condenser and adapter must then be replaced by an air condenser.

At 170° the receiver is changed and the fraction which has already distilled removed and labelled—

Light oils. B.P. up to 170° .

Distillation is continued, and at 230° the receiver is again changed and the fraction, which possesses an odour entirely different from that of the light oils, is labelled

Carbolic oil. B.P. 170° – 230° .

Between 230° and 270° another fraction is obtained which should be labelled

Cresote oil. B.P. 230° – 270° .

Above 270° the process of distillation becomes rather difficult and it may be necessary to heat the flask by means

of several burners, care being taken that in the event of its cracking the boiling pitch shall not come into contact with the skin.

The liquid which now distils has a reddish colour and exhibits a tendency to solidify in the condenser. When the thermometer registers about 330° the process may be stopped, and the final fraction, which should partially solidify on cooling, removed and labelled

Anthracene oil. B.P. above 270° .

The pitch which remains in the flask should then be poured out on to an iron tray and allowed to solidify. The product will be found to be very brittle and may readily be removed from the tray. It forms about 50 to 60 per cent. of the original tar, and contains large amounts of finely divided carbon, but also 20 or 30 per cent. of unsaturated hydrocarbons of extremely high molecular weight.

Separation of the various Hydrocarbons in the Light Oil.—The light oil boiling up to 170° must be separated in a tap funnel from the water with which it is contaminated.

The ammonia and pyridine bases which it may still contain are then removed by shaking once or twice with dilute sulphuric acid, the excess of acid removed by washing with water and the remaining oil dried over calcium chloride. It is then distilled from an ordinary distilling flask, using at first a water condenser, filter flask, etc. That portion which distils above 170° is collected separately and added to the carbolic oil fraction.

The first fraction, B.P. up to 170° , is shaken in a separating funnel with about 5 per cent. of its volume of cold concentrated sulphuric acid, whereby unsaturated compounds are converted into esters of sulphuric acid and phenols are sulphonated; some of the sulphur compounds are also dissolved.

Both the oil and sulphuric acid turn red and sulphur dioxide is evolved. The sulphuric acid is then run off and the operation repeated with some fresh sulphuric acid till the red coloration disappears or becomes much less pronounced. Excess of sulphuric acid is removed by washing with water and the remaining oil is distilled in a current of steam. Non-volatile impurities such as resins remain behind, so that the distillate should be colourless. This also serves another object, since the addition of water to the oil which has been extracted with strong sulphuric acid occasionally gives rise to the formation of emulsions which separate very slowly. A current of

steam, however, removes the hydrocarbons at once. The colourless distillate should be separated, thoroughly dried over calcium chloride and fractionated, using a round-bottomed flask with a rather long neck and fitted with a three or four chamber fractionating column which carries a thermometer.

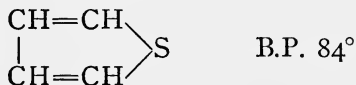
It will be found convenient in the first fractionation of this purified light oil, to collect fractions having roughly the boiling points—

- (I) up to 70° . (II) 70° – 100° . (III) 100° – 125° .
(IV) 125° – 150° . (V) 150° – 170° .

Further fractionation is necessary in order to obtain pure specimens of benzene, toluene, etc.

The residue in the distillation flask, which boils above 170° C., will probably solidify on cooling. It should be removed, pressed out on porous tile to remove oily constituents, dissolved in warm alcohol, filtered if necessary from dirt through a small funnel containing a filter-paper moistened with alcohol, and the filtrate allowed to crystallize. The crystals obtained will probably consist of naphthalene, and melt at 80° .

Benzene obtained from coal tar contains the substance thiophen—



The presence of this substance is detected by placing a crystal of isatin on a white glazed tile, adding one drop of concentrated sulphuric acid and a drop of the benzene, when a blue coloration is obtained (indophenin reaction).

Although the light oils obtained from coal tar are very easily distinguished from shale naphtha and petroleum spirit by chemical processes such as nitration, a very simple test for coal tar naphtha consists in observing its solvent action on coal tar pitch, in which case a dark brown solution is obtained. Petroleum spirit and shale naphtha are without action on this substance. This test may, in fact, be employed to detect more than 5 per cent. of benzene in the other oils.

Separation of the Constituents of the Carbolic Oil.—The carbolic oil which distilled between 170° and 230° , together with that portion of the original "Light Oil," which on re-distillation was found to boil above 170° , should be allowed to stand. A certain amount of naphthalene C_{10}H_8 will be

deposited, but its separation will be much accelerated if the carbolic oil be cooled with ice.

The deposited crystals should be removed and drained on porous tile, after which their purification can be effected by recrystallization from methylated spirits. Naphthalene melts at 80° .

The carbolic oil from which the naphthalene has been deposited (a fairly large amount probably remains in solution, however) is shaken up vigorously in a large separating funnel with successive quantities of 10 per cent. caustic soda solution, about 50 to 60 c.c. being employed each time.

After the addition of the first portion, it may be difficult to see where the line of separation between carbolic oil and alkaline phenol solution occurs; moreover, the two layers may not separate for some time. Finally, however, the tap is opened, and liquid allowed to flow out *slowly* from the funnel. Although dark-coloured, it will be clear and transparent in thin layers. As soon, however, as the line of demarcation is reached, the issuing liquid becomes opaque and oily, and the tap is closed. The second portion of 50 c.c. sodium hydroxide solution is then added, and the operations repeated several times. After three or four extractions, the quantity of caustic soda may be somewhat diminished. The extractions should be stopped when, on acidification of a portion of the last alkaline extract, practically no turbidity due to liberated phenols occurs.

The alkaline extracts are then united and slightly acidified by the VERY CAUTIOUS addition of small quantities of concentrated sulphuric acid, the liquid being well stirred. When a portion of the well-mixed liquid becomes permanently acid to litmus paper, the addition is stopped. Concentrated sulphuric acid is used, since otherwise, by the use of diluted acid, the liquid would become too bulky.

If the quantity of sodium hydroxide contained in the alkaline liquor be known, the theoretical amount of sulphuric acid necessary for its neutralization may be calculated. Too strong acidification of the extract is thereby avoided.

After the addition of sulphuric acid is complete, a dark-coloured oil will be found to have separated and risen to the surface. This consists principally of phenol C_6H_5OH , the three cresols $C_6H_4(OH)CH_3$ and the xylenols $C_6H_3(CH_3)_2.OH$. Traces of the naphthols or hydroxynaphthalenes $C_{10}H_7.OH$ are also present. After the aqueous lower layer has become clear, which indicates that all suspended oil has risen to the surface, it is separated by means of a tap-funnel. Further

small quantities of phenols may be obtained by extracting this aqueous liquor with ether, but the quantity will probably be small, and it will be found convenient to reject the *clear* aqueous layer after separation.

A small quantity of ether is then added to the dark-coloured mixture of phenols, any water which separates being run off from the tap-funnel. A small amount of anhydrous sodium sulphate is then added, and the mixture vigorously shaken. This is repeated several times, after which the ether-phenol mixture is allowed to stand over a fresh and larger quantity of anhydrous sodium sulphate for twenty-four hours.

The dried liquid is then poured off from the sodium sulphate, and the ether removed as far as possible on the water-bath, the usual precautions being observed. The last traces of the ether must be removed by heating over a wire gauze. Between 40° and 100° a certain amount of low-boiling impurities present in the phenols may distil, but above 100° , the thermometer rises rapidly, and the water-condenser must be exchanged for an air-condenser.

Four fractions should now be collected—

- (i) up to 186° .
- (ii) 186° – 196° .
- (iii) 196° – 206° .
- (iv) above 206° .

These should then be re-distilled from a round-bottomed flask, fitted with a fractionating column containing not less than four chambers. The flask must be heated over a free flame, since by this means a much more satisfactory regulation of the distillation is assured. The liquid should be allowed to distil at the rate of about one to two drops per second.

The boiling point of pure phenol is 181° , and the thermometer will probably remain constant at a temperature slightly above this for some time, the fraction coming over during this period being collected separately.

The phenols in the carbolic and creosote oils may be estimated by means of a flask with a long graduated neck as described on page 217.

CHAPTER XVII

METHODS OF HYDROGENATION

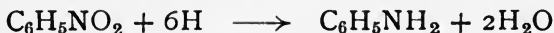
DURING the last fifteen years a great advance has taken place in the methods which the chemist has at his disposal for bringing about the reaction of hydrogen with organic compounds. Up to about 1895, the combination of a substance with hydrogen was usually effected by treating it with such reagents as sodium amalgam and water, tin and hydrochloric acid, sodium and alcohol or electrolytically produced hydrogen. These methods are open to the objection that they involve the use of acid or alkaline solutions; certain organic substances are very sensitive to the action of such solutions, and are readily decomposed by them. In such cases the course of the reaction with hydrogen would be obscured.

Before considering the more recent work on the subject, it will be well to draw some sort of distinction between the use of the words "hydrogenation" and "reduction" as applied to organic compounds.

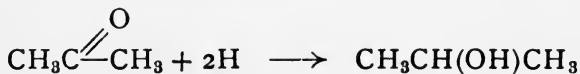
A substance may be said to be hydrogenated when it is caused to take up hydrogen irrespective of whether oxygen is lost at the same time or not.

Nevertheless, the term "hydrogenation" should be restricted to those reactions in which hydrogen is added on to a compound without the simultaneous removal of other elements, or, which is just as important, the production of profound changes in the type of the compound.

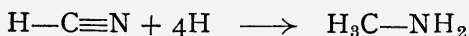
The change of benzene C_6H_6 to hexahydrobenzene C_6H_{12} , of acetylene C_2H_2 to ethane C_2H_6 and of oleic acid to stearic acid, are processes of hydrogenation. On the other hand, such reactions as the conversion of nitrobenzene to aniline—



of acetone to isopropylalcohol—



or of hydrocyanic acid to methylamine—



should be known as “reductions.”

In the last two examples, no elements are eliminated during the change, but the reaction results in each case in the production of an entirely different type of compound—



The preparation of hexahydrotoluene from toluene and hydrogen under the influence of nickel (as described on page 251) is not to be looked upon as a single isolated reaction, but rather as a practical illustration of a great principle, now recognized by all chemists. This is, that in presence of certain finely divided metals, an enormous number of compounds differing widely in their chemical constitution, can be made to combine with hydrogen under conditions where, in the absence of the finely divided metal, no noticeable reaction would take place.

The substance to the presence of which the reaction is *apparently* due is known as a Catalyser, and the resulting change is known as a catalytic action. The catalyser employed seems to undergo no change, although in time its activity may diminish. On its removal the reaction ceases.

Not all catalytic actions involve the presence of hydrogen; an enormous number of widely differing reactions in which hydrogen plays no part are capable of being influenced by catalysers.

From a consideration of the Principle of the Conservation of Energy, it follows that the catalyser cannot be the *cause* of the reaction, otherwise by alternately introducing and removing it, the reaction could be initiated or stopped an indefinite number of times, *i.e.* an indefinite amount of work could be obtained from a system remaining at constant temperature. Such a condition is contrary to all experience.

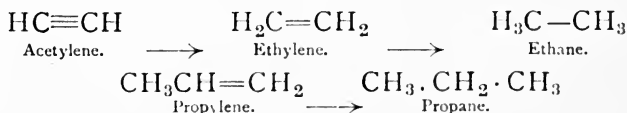
The present-day explanation of such phenomena is that the reaction which is *apparently started* by the introduction of the catalyser is really proceeding at an extremely slow rate, even in its absence, and that the so-called contact effect is simply due to an *acceleration* of this slow reaction.

CATALYTIC HYDROGENATION IN PRESENCE OF NICKEL.

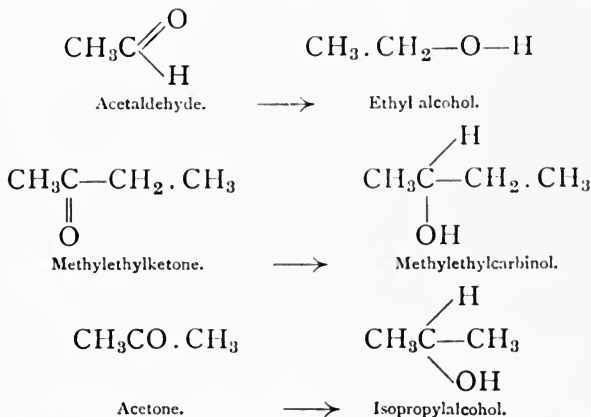
The influence of finely divided nickel on the course of the reaction between hydrogen and various organic substances was first investigated by Sabatier and Senderens in 1896-97, and their researches have been published in a long series of papers in the *Comptes Rendus*.

We may consider a few of their more important results.

(a) Aliphatic Hydrocarbons—



(b) Aldehydes and Ketones.—These compounds are fairly readily converted into the corresponding alcohols. Thus—



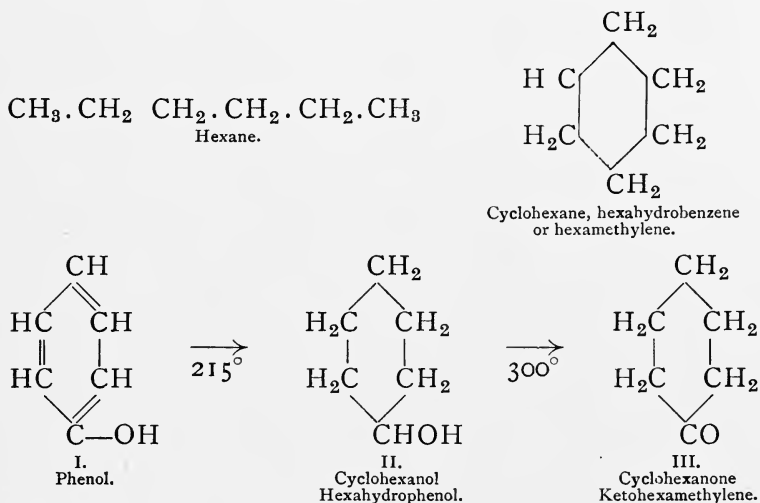
(c) Aromatic Hydrocarbons.—Benzene C_6H_6 and toluene $\text{C}_6\text{H}_5\text{CH}_3$ are converted at 200° into the corresponding hexahydro-compounds C_6H_{12} and C_7H_{14} . Similarly their homologues xylene and cumene take up six atoms of hydrogen under these conditions.

Hexahydrotoluene was found to be identical with the heptanaphthene of Caucasian petroleum, while the hexahydro-derivatives obtained from *o*- and *m*-xylene have also been isolated from crude petroleum.

It is interesting to note that at temperatures above 300° and in presence of finely divided nickel a dehydrogenation occurs and hexahydrotoluene, for example, is converted back into toluene.

(d) **Phenols.**—Ordinary phenol at 215° – 230° is converted into hexahydrophenol (or cyclohexanol). In this case also, above 300° , dehydrogenation of the hexahydrophenol takes place, cyclohexanone or ketohexamethylene being formed, so that in the catalytic hydrogenation of phenol a mixture of II. and III. is obtained. The yield of either product can, however, be made quantitative under suitably chosen conditions.

The relation of these bodies to hexane and cyclohexane is indicated in the subjoined formulæ—



(e) **Aromatic Nitro-compounds** are converted into the corresponding primary amines, *e.g.* nitrobenzene yields aniline.

(f) **The Oxides of Carbon** yield methane when mixed with hydrogen and passed over metallic nickel. With carbon monoxide a temperature of 250° is required, with carbon dioxide, 300° C.

The hydrogen used in all these experiments must be carefully purified since traces of arseniuretted hydrogen, phosphoretted hydrogen, sulphuretted hydrogen or oxygen considerably diminish the activity of the catalyser.

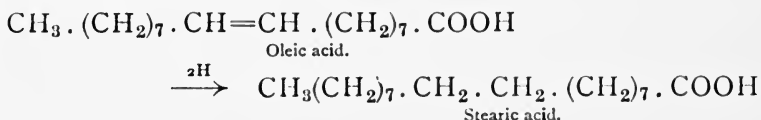
The method of Sabatier and Senderens is particularly useful for the hydrogenation of the stable aromatic hydrocarbons, and in general, of such substances as do not decompose at the comparatively high temperatures employed. Obviously the hydrogenation by this method, of substances which decompose at temperatures above 150° – 200° , is im-

possible. Even, however, in the case of compounds which do not break up at elevated temperatures changes in the position of the double bonds or other linkages in the molecule may occur, giving rise to substances other than those normally to be expected. For instance, although by Sabatier and Senderens' method, acetylene is converted into ethane, the yield is by no means quantitative, a certain amount of benzene is produced. This is a well-known condensation product of acetylene under the influence of heat. Free carbon is also deposited.

If, therefore, it be desired to hydrogenate an unsaturated hydrocarbon (also unsaturated alcohols and ketones), other methods due to Paal and Skita may conveniently be employed, since they do not require high or even slightly elevated temperatures.

Several commercial applications of the Sabatier and Senderens method have been patented.

The German patent, 141029, describes the conversion of oleic acid to stearic acid by mixing the former with nickel powder, heating and passing in hydrogen.



Both these acids are products of fat hydrolysis during soap making. The importance of this patent lies in the fact that stearic acid, which is a solid, is largely used for candle making, while the liquid oleic acid is useless for the purpose. Its ready conversion to stearic acid on a manufacturing scale had not previously been carried out.

In connexion with the technical applications of this method, reference should be made to a paper by C. Ellis, *Journ. Soc. Chem. Ind.*, 1912, page 1155.

CATALYTIC HYDROGENATION IN PRESENCE OF COLLOIDAL SOLUTIONS OF PALLADIUM OR PLATINUM.

A short description must now be given of the methods employed by Paal and Skita for the catalytic hydrogenation of unsaturated substances.

It is well known that ordinary metallic platinum and palladium, especially the last-named metal, are able to occlude or absorb hydrogen. For instance, palladium foil

which has been recently ignited absorbs 370 times its own volume of hydrogen at the ordinary temperature, while, if the electrolysis of acidulated water be performed with a cathode of palladium, the metal absorbs up to 960 times its own volume of hydrogen.

Ordinary platinum absorbs relatively small quantities of hydrogen, but the finely divided metal known as "platinum black" (obtained from solutions of platinum salts by the action of reducing agents such as hydrazine, N_2H_4 , or sodium formate $\text{H} \cdot \text{COONa}$) absorbs more than 100 times its own volume of the gas.

Platinum black and palladium black are capable of causing the catalytic union of hydrogen and oxygen at ordinary temperatures. Since these amorphous metals also occlude oxygen, the explanation is probably to be found in the presence of hydrogen and oxygen in an extremely dense condition on the surface of the catalyser. The case could then be considered analogous to the union of hydrogen and oxygen which takes place under high pressures.

Other reductions can be carried out by means of palladium charged with hydrogen, *e.g.* ferric salts are converted to ferrous compounds, while chlorine and iodine yield the corresponding halogen hydrides.

It has been found that if a *colloidal solution* of metallic palladium is shaken up with hydrogen a considerable amount of the gas is absorbed, the quantity being constant for a given mass of palladium. If, when absorption is complete, an unsaturated substance be added, the absorption of hydrogen begins again and if the compound in question be pure, continues until hydrogenation is complete.

The hydrogen occluded by the colloidal palladium solution is passed over to the unsaturated compound, the palladium itself becoming dehydrogenated. This being so it immediately takes up more hydrogen, again passes it on to the unsaturated substance and so the process continues.

The practical details of the method employed by Skita are given below.* The apparatus is indicated in the diagram Fig. 4I. Hydrogen generated from zinc and dilute sulphuric acid in a Kipp's apparatus is purified by passage through two bottles containing saturated acidified

* Benzene and other aromatic hydrocarbons are not hydrogenated under these conditions. Their hydrogenation to cyclohexane or its derivatives can, however, be effected by adopting certain modifications of the process. For an account of these and of the whole question of catalytic hydrogenation the recent volumes of the "Berichte" of the German Chemical Society should be consulted.

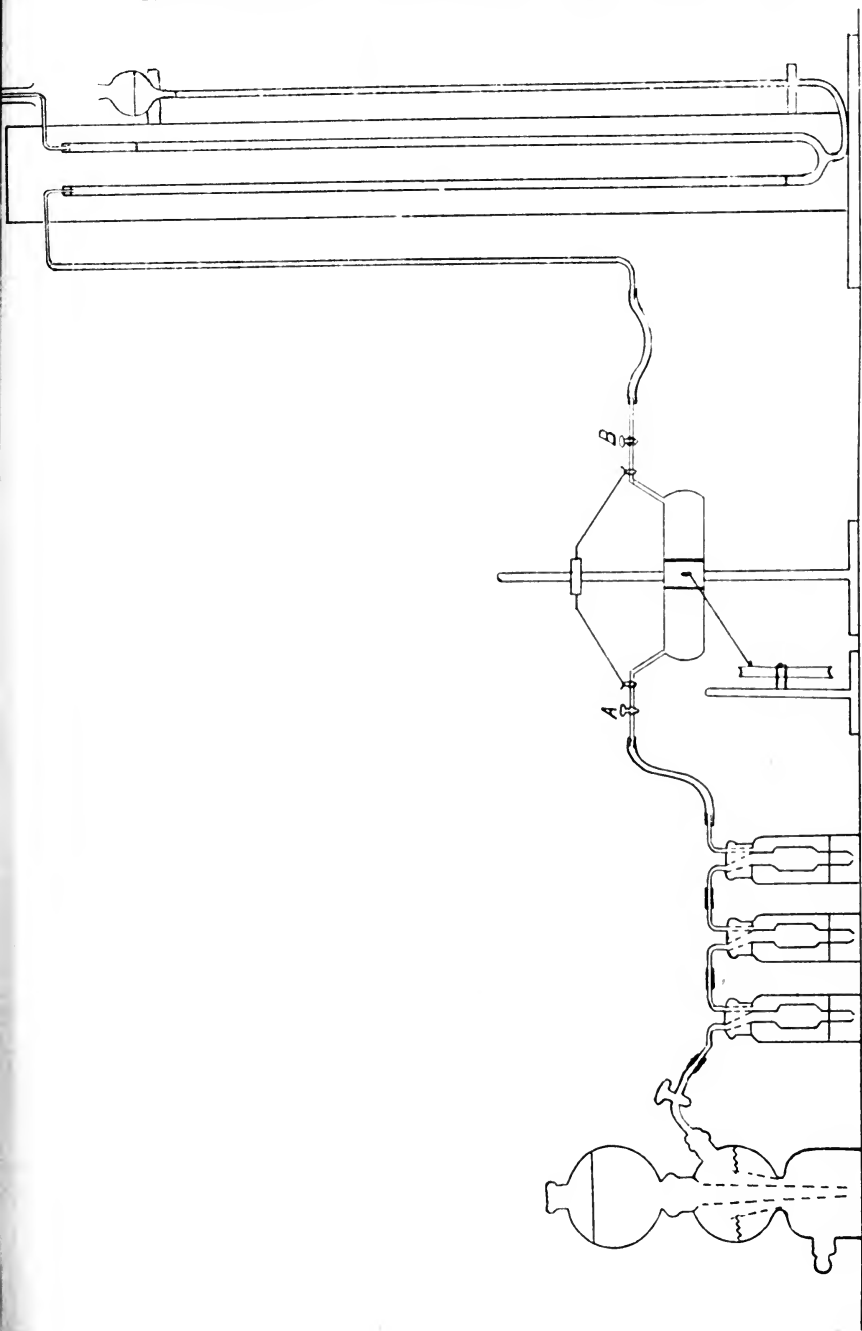


FIG. 41.—Hydrogenation apparatus (Skita).

potassium permanganate solution, and another vessel containing strong potassium hydroxide solution. In order to avoid the frequent refilling of the wash bottles it is advisable to have a layer of potassium permanganate crystals at the bottom of each. It then passes through the cylindrical vessel commonly known as a "Liebig's Duck" (Liebig'sche Ente) to the adjustable manometer from which it escapes into the atmosphere.

A test-tube is placed over the exit tube of the manometer and the purity of the hydrogen ascertained at intervals in the usual way, by removing the test-tube and noting when the gas burns quietly *in the test-tube*. No light may be brought near the absorption vessel or manometer.

As soon as all air is expelled from the apparatus the tube connecting with the wash bottles is closed by means of a clip and disconnected. A small funnel is connected in its place by means of a short piece of rubber tubing. In this funnel and rubber tubing a solution of palladium dichloride containing a trace of gum arabic is placed, and on opening both taps of the cylindrical vessel the solution is allowed to flow into it, care being taken that the level of the water in the manometer is not such as to exert the slightest pressure on the contents of the funnel which will otherwise be ejected. The entry of air bubbles into the apparatus is carefully to be guarded against.

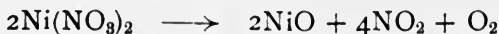
The tap A is then closed, the tube and funnel disconnected, and the vessel shaken vigorously by means of a motor. When the manometer indicates no further absorption of hydrogen, which with 0.1 gram of palladium dichloride and 2 c.c. of a 1 per cent. gum arabic solution usually takes place in about five minutes, the substance to be hydrogenated is introduced into the shaking vessel, the same precautions being observed as during the introduction of the palladium dichloride solution. The wash bottles and Kipp's apparatus are then again connected, and shaking resumed. Absorption takes place, the hydrogen being introduced either from the manometer, in which case tap A is closed, or from the Kipp apparatus directly, when the manometer is shut off by means of tap B. Taps A and B must never be open simultaneously during shaking.

PRACTICAL DETAILS OF THE METHOD OF SABATIER AND
SENDERENS FOR THE HYDROGENATION OF SUB-
STANCES IN PRESENCE OF FINELY DIVIDED NICKEL.

Two or three porous plates (those used for draining crystals and consisting of unglazed earthenware may conveniently be used) are broken up into pieces about the size of peas. Smaller pieces as well as dust should be discarded. The fragments are then boiled with dilute hydrochloric acid for some days till all traces of iron are removed. The hydrochloric acid must be frequently renewed, the fragments being well washed with water before fresh acid is added. Skita ("Katalytische Reduktionen der Organischen Verbindungen," Enke, Stuttgart, page 34) recommends that the fragments be first heated to 300° C. in a stream of hydrogen.

The earthenware is then dried and heated to bright redness, for half an hour or more. This renders the fragments more porous. They are then placed in a very concentrated solution of nickel nitrate which is then evaporated slowly to dryness on the water bath, the mixture being frequently stirred.

The remaining water is driven off in a steam oven, and the impregnated tile fragments are then strongly heated in a nickel tray or dish until all evolution of nitrous fumes ceases and the whole of the nickel nitrate is converted into the oxide.



The nickel oxide must now be reduced to the metallic condition. This is most conveniently carried out in the same apparatus as is employed for the actual hydrogenation, and with carefully purified hydrogen.

The apparatus, Fig. 42, and method of purification of the hydrogen must now be described.

The gas, generated by the action of zinc on dilute sulphuric acid in a Kipp's apparatus bubbles through a series of wash bottles. The first two contain acidified saturated potassium permanganate solutions containing a layer of crystals at the bottom, the next strong sodium hydroxide solution, and the last concentrated sulphuric acid. The hydrogen then passes through a tube of hard glass, A, about 20 centimetres long, containing palladinized asbestos* to a

* Palladinized asbestos may be obtained in the following manner: A convenient amount, about 0.5 gram of palladious chloride PdCl_2 , is dissolved in water with the aid of a little pure sodium chloride with which it forms a more soluble

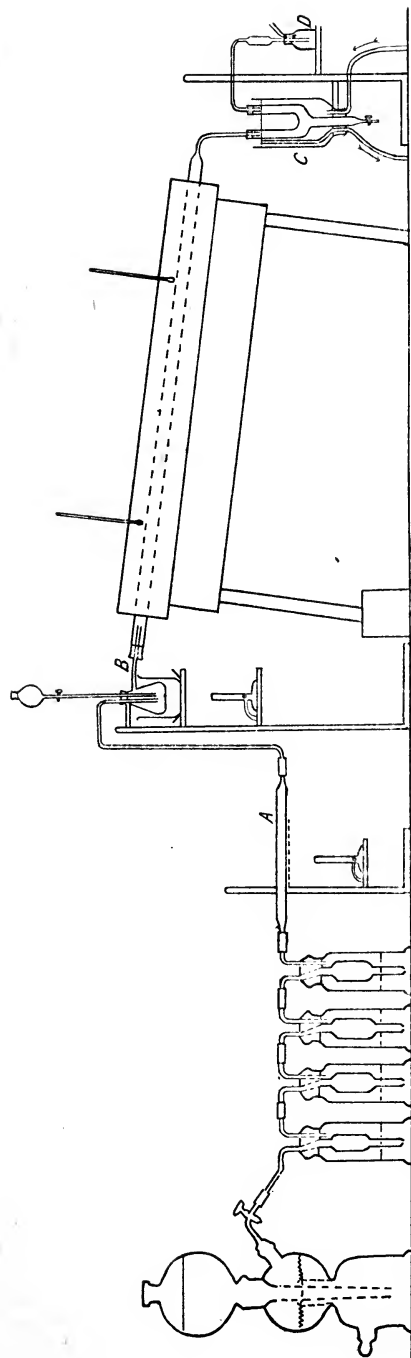


FIG. 42.—Hydrogenation apparatus (Sabatier and Senderens).

small filter flask B, fitted with a dropping funnel. The side tube is connected to the hydrogenation tube, which should be about 1 metre long and 2 centimetres internal diameter. At the further end of this a U-tube, C, fitted with a suitable tap, and cooled by means of a water jacket as indicated in the figure, is attached; this tube in turn connects with a small wash bottle, D, containing a little concentrated sulphuric acid, the exit tube from which is *connected with a good draught*.

The hydrogenation tube is supported in a slanting position either in a furnace or in such a manner that it can be conveniently heated, *e.g.* it may be surrounded by a long iron tube which can itself be heated. The iron tube must contain holes for the insertion of thermometers, the bulbs of which should be in close proximity to the tube.

As far as possible all connections between the various tubes and wash bottles should be made with glass. The minimum quantity of rubber tubing is desirable in order to avoid leakage of hydrogen or diffusion of air into the apparatus.

The reduction of the nickel oxide is carried out by loosely filling the tube with the impregnated tile fragments, and passing hydrogen slowly through the apparatus *till all air is expelled*.

This precaution is most essential, otherwise an explosion will occur on heating.

When, but not before, the apparatus is full of hydrogen, the tube is heated up to about 300° C., when reduction of the nickel oxide takes place. When no more water condenses in the receiver the reduction is complete.



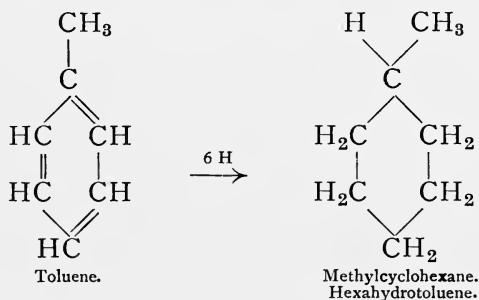
In order to carry out the hydrogenation of toluene, about 50 c.c. are introduced into B by means of the tap funnel, the stem of which is always kept full of liquid; * at the same time the temperature of the tube is lowered and kept constant

double salt, $\text{PdCl}_2 \cdot 2\text{NaCl}$. Slight excess of a cold saturated solution of sodium formate is added, and then sodium carbonate, till the mixture is strongly alkaline. Place in the solution some long fibred, soft asbestos, which will absorb nearly the whole of the liquid and evaporate the mixture to dryness on the water bath. Metallic palladium will separate evenly on the asbestos in a black, finely divided form ($\text{Na}_2\text{PdCl}_4 + \text{H} \cdot \text{COONa} = 3\text{NaCl} + \text{HCl} + \text{CO}_2 + \text{Pd}$). When the asbestos is dry the sodium chloride is completely washed out with water and the product again dried, when it is ready for use.

* As an alternative method of introducing the toluene, the hydrogenation tube may be fitted with a rubber stopper carrying two tubes, through one of which the hydrogen enters, the toluene in the liquid form being introduced through the other from a burette.

at 200°. As the hydrogen bubbles through B it vaporizes the toluene, which on passage through H is partially hydrogenated. The speed of the hydrogen should be such that 50–100 c.c. escape from the wash bottle D per minute. If the rate be greater the toluene vapour will not remain long enough in contact with the catalyser.

The volatilization of the toluene is facilitated by surrounding B with a beaker of heavy mineral oil (B.P. above 300°) kept hot on a sand-bath.



It will probably be found necessary to pass the specimen of toluene two or three times through the apparatus before hydrogenation is complete.

In order to follow the course of the reaction a small quantity of the liquid which condenses in C may from time to time be tested by cautiously and slowly adding it to a small quantity of fuming sulphuric acid which is kept cool by water and well shaken after each addition. Toluene dissolves with the formation of isomeric toluenesulphonic acids, the relative amounts of which depend on the temperature at which the sulphonation is conducted. For example—

	at 0°	at 100°
<i>o</i> -toluene sulphonic acid	42·7 per cent.	17·4 per cent.
<i>m</i> - " " "	3·8 " "	10·1 " "
<i>p</i> - " " "	53·5 " "	72·5 " "

Hexahydrotoluene, on the other hand, is unattacked, and after the toluene has dissolved may be separated from the acid liquid in a tap funnel, washed with water, dried over calcium chloride and distilled. It boils at 102°–104°. The yield is usually about 90 per cent. of that theoretically obtainable.

CHAPTER XVIII

ALCOHOL

THE CHEMISTRY OF ALCOHOLIC FERMENTATION.

WHEN moist barley grains are kept at a temperature of 10° – 20° C. for a time, germination (sprouting) begins. After this process has continued for some hours it can be shown that the starch (which forms by far the largest proportion of the barley) is being gradually converted into sugar, and as a matter of fact, that particular sugar known as maltose or malt sugar ($C_{12}H_{22}O_{11}$). Simultaneously the nitrogenous organic matter (protein substances) which is also present in the grain begins to decompose into simpler products, and finally into amino-acids.

If the germination be arrested by gently heating to about 40° C. before too much of the starch has disappeared, and the resulting malt be extracted at ordinary or only slightly elevated temperatures with water or alcohol, a solution is obtained which possesses very remarkable properties.

If added to some starch paste, preferably kept between 40° and 60° C., the starch is rapidly converted into maltose (certain complicated substances such as dextrin and malto-dextrin are also formed), and ceases to give a blue colour with a solution of iodine in potassium iodide. An extract prepared in a similar manner from unmalted barley is quite devoid of this action on starch.

Further investigations into the processes concerned in the production of malt have shown that the formation of sugar during germination is due to the production within the grain of a substance to which the name *Diastase* has been given.

This substance is able to convert starch into maltose or malt sugar, either within the grain or when dissolved in water and brought into contact with starch paste.

Diastase is not produced in the starchy part of the barley grain. Before it can reach the starch and attack it the cell wall which separates them must be dissolved by the agency

of another substance which is simultaneously produced, called *Cytase*.

Both *cytase* and *diastase* are included in the class of substances known as *Enzymes*, to the action of which very many of the chemical changes occurring in plant and animal organisms are to be ascribed.

The breaking down of fat in the animal organism is an example of enzyme action, which in this instance is reversible. Extracts of fatty tissues have been shown to be capable of breaking down fats into glycerol and the appropriate fatty acid (see page 38). An equilibrium is, however, obtained since fats can be directly synthesized from glycerol, fatty acids and tissue extract.

The particular enzyme responsible for these actions is known as *Lipase*.

The formation of glucose, prussic acid and benzaldehyde

$\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$, in the bitter almond has been conclusively proved

to be due to the action of an enzyme *emulsin* or *emulsase*, contained in the tissue of the almond, on a complex nitrogenous organic compound known as amygdalin which is also contained therein. The same action can be made to take place in the test-tube between pure amygdalin and almond extract.

The production of the so-called autumn tints in the leaves of certain trees, *e.g.* the pear tree, is probably due to the action of one or more oxidizing enzymes (the so-called oxydases) on quinol (hydroquinone) produced therein. The ready darkening of hydroquinone owing to atmospheric oxidation is familiar to most photographers.* See *Journ. Chem. Soc., Abstracts*, 1911, Section II. p. 144.

We may for the moment defer a consideration of the chemical nature of these enzymes, and having now realized the wide scope of their activities, may deal briefly with those particular cases of enzyme action which are met with in the alcoholic fermentation of sugar.

If the malt grains after heating are macerated with water at about 60° C., the change from starch to maltose under the influence of the diastase is quickly completed. If after cooling to about 20° C. yeast be added, the well-known phenomena of fermentation are observed, carbon dioxide is evolved, sugar disappears, and alcohol is produced, which can be isolated from the mixture by distillation.

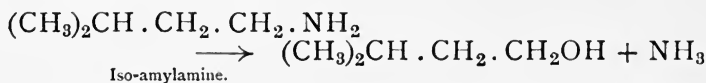
* Compare also Brooks, "The Rôle of Oxydases in the Formation of Certain Constituents of Essential Oils," *Journal of Amer. Chem. Society*, 1912, 34, 67.

Glycerol, $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$, succinic acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ and a mixture of alcohols of the series $\text{C}_n\text{H}_{2n+1}\text{OH}$, known as fusel oil, are also produced in relatively small quantities. The mechanism of the formation of some of these bye-products is not thoroughly understood. It is possible that the glycerol results from the action of an enzyme of the lipase type (see page 256) on fatty matter (present in the yeast itself) which, in presence of such an enzyme would be hydrolysed, giving rise to glycerol and an acid of the series $\text{C}_n\text{H}_{2n+1}\text{COOH}$.

"Fusel oil" consists of a mixture of two isomeric amyl alcohols $(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$ and $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CH}_2\text{OH} \\ \diagdown \\ \text{CH}_3\text{CH}_2 \end{array}$ together with a certain amount of *n*-propylalcohol $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$.

The work of Felix Ehrlich has recently shown that some of the alcohols of fusel oil result from the action of yeast on amines and amino-acids, derived from the breaking down of the more complex nitrogenous organic matter present in the fermenting liquid.

Thus iso-amylamine has been shown to yield iso-amyl alcohol under the influence of yeasts.



It is fairly certain that a pure, well-nourished and active yeast plant will give rise to less fusel oil and glycerol than a weaker one; moreover, the production of the higher alcohols $\text{C}_n\text{H}_{2n+1}\text{OH}$ is always greater towards the end of a fermentation.

Bacteria are also able to produce fusel oil from the above-mentioned nitrogenous compounds.

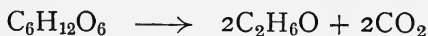
The small amounts of acetaldehyde and acetic acid which are often present in the liquor resulting from the fermentation of sugar by yeast are usually due to secondary decompositions (oxidations).

The careful work of many biochemists has established that the yeast contains an enzyme known as *maltase* (also present in malt), which converts the maltose not directly to alcohol but to glucose $\text{C}_6\text{H}_{12}\text{O}_6$.



The final step, glucose $\longrightarrow \text{CO}_2$ and alcohol, is the work of another enzyme, *zymase*, also contained in yeast.

Alcoholic fermentation is thus seen to be an extremely complicated process; neglecting intermediate stages the production of alcohol from glucose may however be represented thus—



Chemical Properties of Enzymes.—Enzymes can frequently be precipitated from tissue extracts by means of alcohol. Probably very few, if any, enzymes have as yet been obtained in a pure condition, mineral, protein, or carbohydrate matter being usually present even in the best preparations. Consequently very little is known of their chemical constitution. They are probably optically active and allied both to the proteins and the carbohydrates. It has been found that at low temperatures their activity is suspended, to return on regaining normal conditions. Above about 65° C. most enzyme solutions undergo decomposition, coagulate and permanently lose their chemical activity. Traces of certain substances, such as hydrocyanic acid, are sufficient to inhibit their activity. On the other hand, some enzymes appear to be capable of bringing about certain reactions only in the presence of traces of calcium or manganese salts, *e.g.* the blood-clotting enzyme *thrombase* will not coagulate blood from which calcium salts have been removed, but immediately does so when a trace of calcium chloride is added.

Enzyme action is to some extent specific; thus some enzymes are known which will cause the fermentation of glucose, but remain without action on the closely related isomer galactose. These and similar facts have led to the conclusion that there must be a certain relation between the structure of the molecule of the enzyme and that of the substrate (substance it attacks), in order for a reaction to take place. If this relation be absent the enzyme is without effect.

Emil Fischer compares this similarity in structure to that existing between a lock and the key which is able to pass it.

Enzymes, then, are produced by living cells. None have so far been synthesized. The presence of living protoplasm is not, however, essential to their action.

If yeast be ground up with sand, by means of which the cell walls are broken, and the mass be submitted to high pressure, a juice exudes. Any yeast cells floating in this are killed by means of acetone, filtered off, and the absence of life in the filtrate proved by microscopical examination. This liquid, however, still sets up vigorous fermentation in a glucose (grape sugar) solution owing to the zymase it contains.

It is noteworthy also that succinic acid and glycerol are obtained in this cell-free fermentation of sugar just as in the ordinary process where living yeast is present.

PREPARATION OF ALCOHOL FROM POTATOES.

About 5 lbs. of potatoes are taken, peeled, and cut into thin slices. These are then placed in a saucepan along with about two to three litres of water. The mixture is then heated up as rapidly as possible, care being taken that the potatoes do not burn. This is likely to take place when a pulp begins to be formed ; it may, however, be prevented by stirring, and the use of a smaller flame.

As the water in the saucepan evaporates more should be added. When the potatoes have been reduced to the consistency of a thin cream, and solid lumps have disappeared, a portion of the resulting starch paste is cooled, and the presence of starch noted by the blue colour produced on addition of a few drops of a solution of iodine in potassium iodide.

About 25 c.c. of extract of malt* is now added to the main bulk, but NOT UNTIL THE TEMPERATURE HAS FALLEN BELOW 60° C. The mixture is well stirred and set aside for an hour or so, at the end of which time it is again tested with iodine. Starch is found to be absent. [The hydrolysis† of the starch to glucose may also be carried out directly by boiling with dilute acids. This method is largely used for the cheap manufacture of glucose, which, when prepared in this way, frequently contains traces of arsenic, derived from the sulphuric acid employed.]

A little yeast‡ is then added to the resulting sugar solution, which must not be at a temperature of more than 25° C. and should be placed in a capacious tall vessel, which should not be more than one-third full. The mixture is then covered up and set aside to ferment for about thirty hours. The yeast multiplies, much frothing occurs and a thick scum of yeast rises to the surface.

When all fermentation has ceased and the liquid has become quiescent, it is introduced into a large flask which

* Any good medicinal preparation of malt extract may be used, except those containing cod-liver oil.

† The term "hydrolysis" as used here indicates the reaction undergone by an organic compound on taking up or interacting with the elements of water, usually with the formation of simpler substances, compare hydrolysis of esters, page 39.

‡ Ten to fifteen grams are ample, and probably much more than enough.

must not be more than half full, a little sodium hydroxide added to fix dissolved carbon dioxide and also a few grams of tannic acid. Both these agencies diminish frothing during the subsequent distillation. The flask is connected to a condenser and the mixture cautiously distilled till a few drops of the aqueous distillate evolve no inflammable vapour on boiling. This distillate is preferably to be collected in three separate portions of about equal volume; the first is very rich in alcohol, especially if the distillation has been conducted slowly.

The first distillate is now placed in a round-bottomed flask fitted with a small fractionating column, bearing a thermometer and connected with a water condenser. The re-distillation process is then started and continued for about ten to fifteen minutes after a few drops of the distillate cease to yield an inflammable vapour on being boiled. The watery liquid remaining in the distillation flask is now thrown away.

The process is repeated with the second and third original distillates, the alcohol which they yield being collected in the same receiver as that from the first distillate.

The volume of the total aqueous alcohol is now measured and the specific gravity taken. From the result so obtained the percentage of alcohol present may be calculated and hence the amount of alcohol produced from the weight of potatoes taken.

Some lumps of fresh quicklime* are now added to the aqueous alcohol (in some cases a third distillation with a fractionating column may first be necessary) in such quantity as to rise slightly above the surface of the liquid.

After allowing the alcohol to stand for a while in contact with the quicklime (preferably over night) it is distilled on the water bath, and that portion coming over between 78° – 80° is collected separately.

For data as to the production of alcohol from starch, see page 327.

OTHER METHODS FOR THE PRODUCTION OF ALCOHOL.

(I.) **From Cellulose.**—Ordinary wood contains about 60–70 per cent. of cellulose, a carbohydrate having the empirical formula $C_6H_{10}O_5$, and the molecular weight of which is unknown. The remainder of the woody tissue consists of resins and certain complicated substances such as lignin and xylan.

* Calcium chloride cannot be used since it forms an addition product with alcohol.

The formula of lignin is unknown. The presence of this substance in wood is probably responsible for the formation of methyl alcohol on destructive distillation (see page 276), since pure cellulose does not yield this substance on distillation.

Xylan probably stands in the same relation to the sugar-xylose $C_5H_{10}O_5$ (a pentose), as cellulose does to the hexose glucose $C_6H_{12}O_6$ (see page 26).

Cellulose contains no free carbonyl group, but several hydroxyl groups. With concentrated nitric and sulphuric acid these $-OH$ groups are converted into $-O-NO_2$ groups which are present in the various explosive and inflammable cellulose nitrates such as gun-cotton and collodion.

Much of the cellulose used in such enormous quantities for making paper—filter-paper being almost pure cellulose—is obtained from wood by removing the outer layer of resins, lignin, etc.

In the manufacture of brown paper and news-paper the separation is carried out mechanically by means of suitable disintegrators and pulping machines. The resulting product, however, is never pure and always contains lignin and fragments of wood.

For some of the finer kinds of paper the cellulose is obtained by heating wood with a solution of calcium hydrogen sulphite $Ca(HSO_3)_2$ containing sulphurous acid. This dissolves the resinous and other substances, the presence of which is detrimental to the quality of the paper. The unchanged cellulose fibres remaining behind are then filtered and washed.

The spent sulphite liquor is known as "waste sulphite lye," and contains over 50 per cent. of the weight of the wood in the form of the calcium salt of the so-called ligninsulphonic acid. As might readily be expected, the formation of this complex substance is accompanied by several other reactions, certain of which result in the partial hydrolysis of some of the cellulose giving rise to glucose $C_6H_{12}O_6$. The xylan similarly yields the pentose xylose $C_5H_{10}O_5$. Acetic acid, tannins and ill-defined resinous and gummy substances are also produced.

The satisfactory utilization of this waste lye has been the subject of much research, since when it is allowed to flow away into rivers considerable pollution occurs.

In Sweden, where the sulphite process for cellulose is largely carried out, attempts have been made to ferment the glucose contained in the lye, thus giving rise to alcohol.

One ton of wood gives rise to about ten tons of waste lye which contains about one per cent. of fermentable sugar.

The lye is aerated and neutralized with calcium carbonate or with lime, yeast added, and the mixture allowed to ferment, after which it is distilled in the usual way. About six litres of absolute alcohol may be obtained from 1000 litres of the lye, corresponding to about 5-6 per cent. by weight of the original wood.

The alcohol obtained contains a certain amount of methyl alcohol as well as traces of other volatile substances, and so is obtained directly in a conveniently denatured condition.

It will have been noticed that the process just described consists in the production of alcohol from the glucose which has arisen as a bye-product in the manufacture of pure cellulose.

Numerous attempts have been made to convert cellulose directly and quantitatively into glucose on a manufacturing scale.

When purified cellulose is treated with concentrated sulphuric acid, it dissolves to form a soluble intermediate product which, on dilution of the acid with water to a two per cent. strength and heating to 120° under pressure, is readily converted into glucose; this, after the acid present has been neutralized, can be fermented.

It is obvious, however, that it would be much more satisfactory if the intermediate isolation of the cellulose could be dispensed with. Consequently, another method has been devised in which sawdust is heated directly with dilute sulphuric acid under high pressure, by which means the cellulose which it contains is converted into glucose.

In both these processes, however, the yield of alcohol is poor, being only 15 per cent. of the original cellulose, or 6 per cent. on the weight of the wood. This is due to the fact that at the high temperature and pressure necessarily employed the glucose undergoes further change into substances which are not capable of being fermented.

Cohoe (*Fourn. Soc. Chem. Ind.*, 1912, p. 513) describes certain experiments in which he has employed hydrochloric acid as the hydrolyzing agent instead of dilute sulphuric acid, both on the small scale and in a fairly large digester.

Sawdust was heated with hydrochloric acid at 125° - 150° C. in sealed tubes contained in an oil bath. A yield of 25-29 per cent. of sugars was obtained. By washing out the sugar with water and treating the sawdust again with acid and repeating the operation several times, a yield of as much as 60 per cent. of sugar, calculated on the weight of dry sawdust taken, could be obtained.

Cohoe considers that hydrochloric acid is to be preferred

to other acids as giving a better yield of glucose. He also states that coarse sawdust gives better results than fine, and that valuable bye-products, such as turpentine, are recoverable by his method.

It is worthy of note that quite recently, Willstätter and Zechmeister (*Berichte der Deutschen Chemischen Gesellschaft*, 1913, 46, 2401), by hydrolyzing cellulose with hydrochloric acid containing 40–42 per cent. of hydrogen chloride, have obtained a theoretical yield of glucose. Their results, therefore, must be accepted as further evidence of the importance of Cohoe's work.

Several patents have been taken out in Germany by Classen with a view to the production of alcohol from wood, e.g. D.R.P. 111868, 118540, 121869, 123911 and 130980.

In the case of the last-mentioned patent, 100 kilograms of wood containing about 25 per cent. of moisture are mixed with 30–35 kilograms of an aqueous solution of sulphurous acid containing about 9 per cent. of sulphur dioxide. The saturated mass is then heated in suitable digesters fitted with a stirring arrangement to 120°–145°. After about an hour any sulphur dioxide remaining is allowed to escape; traces being finally removed by boiling the residue with water. After neutralization the resulting liquid is fermented. About 25 per cent. of the wood is stated to go into solution, and of this 90 per cent. is fermentable.

The Lignum Inversion Company of Chicago employs a modification of Classen's method in which 100 kilograms of wood, when heated to 165° C. with 3 per cent. sulphurous acid under 7 atmospheres pressure, can be made to yield about 12 litres of pure alcohol.

(II.) **From other Substances.**—For preparation of alcohol from ozone, acetylene and hydrogen at low temperatures, see D.R.P. 149893.

For the Arachequenne method from ethylene, which is converted into ethylsulphuric acid which, with water, yields alcohol, see "Modern Industrial Chemistry," Blucher, page 23.

Properties of Alcohol.—Ethyl alcohol when perfectly pure is a colourless, very mobile liquid which possesses a characteristic odour and a burning taste. It boils at 78° and has a specific gravity of 0.806 at 0°. It can be caused to solidify by means of liquid air, and forms a crystalline mass melting at –114°.

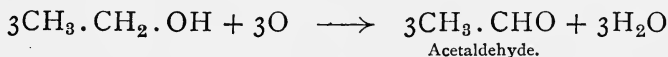
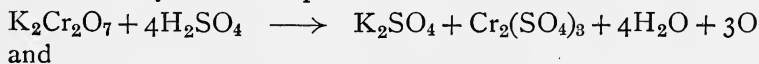
When free from moisture and perfectly pure it is known as absolute alcohol. In this form it is very hygroscopic. Traces of moisture can readily be detected in alcohol by the

addition of dehydrated copper sulphate, which gradually becomes blue, even if only very minute quantities of water are present.

It is, unlike the higher members of the series $C_nH_{2n+1}OH$, miscible with water in all proportions; a rise of temperature and a contraction in volume taking place. The contraction is greatest when 48 parts by volume of water are added to 52 parts by volume of absolute alcohol, the resulting mixture having a volume of only 96.3 at 20°. If alcohol be mixed with snow in the proportion of 2 : 1, the temperature of the mixture falls to $-21^{\circ}C.$ ($-5.8^{\circ}F.$). The determination of the percentage of water in alcohol or *vice versa* is best carried out by means of an accurate hydrometer or specific gravity bottle. Tables* have been prepared as a result of very painstaking experiments showing the specific gravities of mixtures of alcohol and water in proportions varying from 0 to 100 per cent. at all temperatures between 0° and 30°. When the specific gravity of a specimen of aqueous alcohol at a given temperature is known, the percentage of alcohol contained therein can be read off by reference to the table.

Two useful tests for alcohol may be given here.

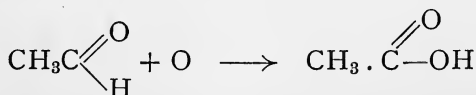
(i) To an aqueous solution containing alcohol a few drops of a solution of potassium dichromate acidified with sulphuric acid are added. On warming the mixture the orange-coloured potassium dichromate will be reduced to the green chromium sulphate, and at the same time the characteristic fruity odour of acetaldehyde will be produced.



The liberation of oxygen by the action of sulphuric acid on potassium dichromate is better understood if the equation be written—



If the acidified potassium dichromate be in excess and the action be prolonged, the acetaldehyde is converted into acetic acid.

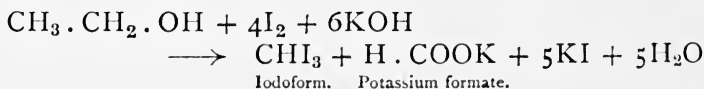


* For tables see Clowes and Coleman: "Quantitative Analysis."

Certain other alcohols such as methyl, propyl, butyl and amyl alcohols, as well as many other organic substances of widely differing types, also reduce potassium dichromate.

(ii) **The Iodoform Test.**—The liquid which is suspected to contain alcohol is treated with potassium hydroxide, warmed to 60° C., and a solution of iodine in potassium iodide added drop by drop.

A yellow crystalline precipitate is thrown down, though only slowly if the solution be dilute. This is iodoform or tri-iodomethane CHI_3 . Its formation may be represented thus—



The reaction probably occurs, however, in several stages, intermediate products, not appearing in the above equation, being formed.

Acetone $\text{CH}_3 \cdot \text{C} \cdot \text{CH}_3$ and many substances containing



the group $\text{CH}_3 \cdot \text{C}$ in union with oxygen, whether present as a CO or as an —OH group, also answer this test (see page 278).

Iodoform has a peculiar and characteristic smell, and is largely used as an antiseptic in surgery.

Proof Spirit.—This is defined by Act of Parliament to be “such a spirit as shall at a temperature of 51° F. weigh exactly $\frac{1}{3}$ of an equal measure of distilled water.” Such a spirit contains 49·3 per cent. by weight of alcohol and 57·1 per cent. by volume.

Originally “proof spirit” was defined to be alcohol of such a strength that when gunpowder was moistened with it and a light applied it was just possible to set fire to the powder. If no ignition of the gunpowder took place the spirit was said to be *under proof*; when ignition readily occurred, *over proof*.

A spirit 5° under proof would contain in each 100 volumes as much alcohol as 95 volumes of proof spirit; similarly 100 volumes of a spirit 5° over proof would contain as much alcohol as 105 volumes of proof spirit.

In all other European countries the strength of alcohol is more rationally expressed as the number of litres of absolute alcohol contained in 100 litres of the aqueous mixture.

The flame of burning alcohol is only slightly luminous

and does not deposit soot, and is thus eminently suitable for heating purposes and for use with incandescent mantles.

Duty on Alcohol.—The Customs authorities of Great Britain levy a duty on alcohol of 14s. 9d. per gallon of proof spirit. In the United States of America the tax is \$1.10 per gallon of 50 per cent. alcohol (by volume) or \$2.07 per standard gallon, which represents 231 cubic inches of 94 per cent. alcohol (by volume).

Owing, however, to the importance of alcohol in many manufacturing processes and its suitability for domestic operations such as cooking and heating, it is very desirable that alcohol should be obtainable at a less prohibitive price. This being so it is obviously essential that the public should not be able to use as a beverage any alcohol supplied under advantageous terms for such special purposes.

The Governments of practically all civilized countries have therefore adopted various processes for "denaturing" the alcohol, *i.e.* of adding to it some substance or substances which on account of their taste, odour, or other property will render the spirit unfit for drinking and may not readily be removed from it.

As will be seen later, the various processes employed differ considerably, but in most cases one of the ingredients employed is crude wood spirit or wood-naphtha (see page 277), the principal constituent of which is methyl alcohol, acetone also being present. The origin of the term methylated spirit, by which denatured alcohol is usually known in this country, is therefore obvious.

Since 1906 the use of duty-free undenatured alcohol has been permitted in the laboratories of Universities and Technical Colleges in Great Britain and Ireland; under special conditions it is also supplied to manufacturers.

CONDITIONS GOVERNING THE USE OF ALCOHOL FOR INDUSTRIAL PURPOSES IN GREAT BRITAIN AND IN GERMANY.

The use of methylated (denatured) spirit free of duty was first authorized in Great Britain in 1855.

"The practice resulting from the Alcohol Laws has been as follows:—

"Up to the year 1855 spirit could not be used duty-free

by the public under any circumstances. From 1855 to 1861 it could be used duty-free for manufacturing purposes only, if methylated according to the prescribed process.

"From 1861 to 1891 spirit could be used duty-free for any purpose other than consumption directly or indirectly as a beverage, or internally as a medicine, provided it was mixed with wood-naphtha, to the extent of one-ninth of its volume. But, if used in large quantities, as for manufacturing purposes, it could not be purchased from a retailer of methylated spirit, but only from a methylator, and the user was subject to Excise supervision.

"From 1891 to 1902, the use of this kind of methylated spirit (which came to be described as 'ordinary' methylated spirit) was confined to manufacturing purposes, subject to the same conditions as before; while for general purposes a spirit consisting of the above spirit with an addition of 0.375 per cent. of mineral naphtha (petroleum)* and known as 'mineralized' methylated spirit, was brought into use. It is only in this spirit that retailers are permitted to deal.

"Since 1902, the two kinds of methylated spirit have continued to be used as before. But an alternative to their use has been opened to manufacturers, under which spirits may be employed after being subjected to some special process of denaturing, appropriate to the particular industry, or possibly even in a pure state, should circumstances be held by the Board of Inland Revenue so to require."

(Report of the Departmental Committee on Industrial Alcohol, 1905.)

In this country the cost of production of methylated spirits is about 11*d.* per gallon, but on account of Excise regulations the price amounts to about 1*s.* 6*d.* per gallon; the retail price is about 2*s.* 0*d.* per gallon.

"The rules and practice of the German Empire may be briefly described as follows:—

"(1) Spirit may be used duty-free in a pure, undenatured state, only in a very limited number of cases, viz.:—

(a) In public, *i.e.* State or municipal hospitals:

(b) In similar scientific institutions:

(c) For making smokeless powder, fuses and fulminates.

"(2) For all other purposes, without exception, duty-paid

* "Wood naphtha" is miscible with aqueous alcohol, but "mineral naphtha," consisting of saturated hydrocarbons of the paraffin series, is not. Consequently, on diluting mineralized methylated spirit with water, a turbidity is produced.

spirit must be used, *unless* the spirit be subjected to some *authorized* process of denaturing prior to use.

“(3) The authorized processes of denaturing fall into two main classes, according as they result in :—

A. Complete Denaturing.

B. Incomplete Denaturing.

“The processes authorized for ‘Complete Denaturing’ are two, viz. :—

(a) An admixture with every 100 litres of spirit of $2\frac{1}{2}$ litres of a mixture containing 4 parts of wood-naphtha and 1 part of pyridine bases. (To this mixture 50 grams of lavender or rosemary oil may be added optionally, to counteract the smell of the pyridine bases. The addition is, however, seldom made.) Spirit thus denatured is what is used for domestic purposes—heating, lighting, and cooking. It is seldom used for industrial purposes. The only purpose of that kind for which its employment is considerable is the manufacture of cheap varnish.

(b) An admixture with the spirit of half the quantity (viz. : $1\frac{1}{4}$ litres per 100 litres of spirit) of the above denaturing mixture, together with an addition of $\frac{1}{4}$ litre of a solution of methyl violet dye, and ‘benzol’ in quantities that may range from 2 to 20 litres to every 100 litres of spirit.

“Although spirit thus treated is classed as completely denatured, its use is limited to agricultural and motor engines, and the process would seem to fall more properly into Class B.

“The spirit thus denatured is largely used in practice for agricultural engines.

“The processes authorized for ‘Incomplete Denaturing’ are numerous. They consist :—

(a) Of two alternative processes of general application, viz. :—

The addition to every 100 litres of spirit of either—
5 litres of wood-naphtha,
or $\frac{1}{2}$ litre of pyridine bases.

(b) Of numerous processes of special application.

“The processes applicable to the most numerous and most important industries, including coal tar colours and chemical preparations, are the four alternatives of—

An addition to every 100 litres of spirit of—

- (1) 10 litres of ethyl ether,
- or (2) 1 litre of benzol, *i.e.* crude benzene containing toluene or xylene,
- or (3) $\frac{1}{2}$ litre of turpentine,
- or (4) 0.025 litre of animal oil.

"The above regulations are applicable only to ethyl alcohol. Methyl alcohol does not fall within the charge to spirit duty in Germany, and may be used freely for industrial purposes, without control by the Revenue authorities."

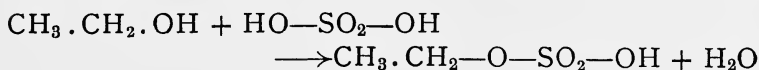
(Report of the Departmental Committee on Industrial Alcohol, 1905.)

CHAPTER XIX

DERIVATIVES OF ETHYL ALCOHOL

PREPARATION OF POTASSIUM ETHYLSULPHATE.

EIGHTY-FOUR grams of absolute alcohol (106 c.c.) are placed in a round-bottomed $\frac{1}{2}$ -litre flask. Sixty grams (33 c.c.) of concentrated sulphuric acid are slowly added and the mixture well shaken. The commencement of a reaction, represented by the equation—



is indicated by the rise in the temperature which is observed. In order to complete the reaction as far as possible the contents of the flask are heated on a water-bath under a reflux-condenser, whereby any alcohol which volatilizes is immediately returned to the flask. The whole apparatus is inclined at an angle of about 45° . This is in order that the steam arising from the water-bath may not be condensed on the outside of the cold condenser and so run down and conceivably soak through the cork into the reaction flask, as would probably be the case if the condenser were placed vertically over the water-bath.

After heating for two or three hours the reaction mixture is cooled and poured into about 500 c.c. of water contained in a large porcelain dish. We must now separate the ethylsulphuric acid from any alcohol which has escaped combination and from any excess of sulphuric acid. To do this we take advantage of the fact that calcium sulphate is almost insoluble in water, whilst calcium ethylsulphate is readily soluble. Calcium carbonate, which has been rubbed into a thin cream with water, is added till the liquid is neutral. Both acids are now present in the form of their calcium salts. The calcium sulphate is filtered off by means of a pump and a large Büchner

funnel and washed with water; the filtrate, which contains calcium ethylsulphate is heated on the water-bath, and the calcium precipitated as calcium carbonate by addition of a solution of potassium carbonate. About 60 grams will be necessary, and this amount should be dissolved in the minimum quantity of hot water. By this means the solution will be prevented from becoming too dilute, and much tedious evaporation will be obviated. (If the precipitation be carried out in the cold the calcium carbonate has a slimy consistency and can be filtered only with difficulty. Heat renders this precipitate granular.) A small quantity of the liquid is then filtered, and the filtrate tested with a few drops of the potassium carbonate solution. If no precipitate be produced, all the calcium has been removed.

Care must be taken not to add too much potassium carbonate, otherwise the final product will be contaminated with this salt.

After the calcium carbonate has been removed by filtration, using a pump and Büchner funnel, the resulting solution of potassium ethylsulphate is concentrated in a large porcelain dish on the water-bath until a portion of the liquid withdrawn on a glass rod, crystallizes on cooling. Any alcohol which may have escaped the action of the sulphuric acid will by now have volatilized.

The crystals which are deposited when the hot concentrated solution is allowed to cool are transferred to a Büchner funnel and washed with methylated spirit.

The potassium ethylsulphate may be purified by heating up with alcohol under a reflux condenser on the water-bath (see under Fractional Crystallization, page 131). The solution is quickly filtered, through a hot-water funnel, from any dirt or insoluble matter, and the filtrate allowed to cool. The crystals which are deposited are filtered through a Büchner funnel and washed once with alcohol.

Ethylsulphuric acid, also known as sulphovinic acid, or ethyl hydrogen sulphate, or the monoethyl ester of sulphuric acid, and its salts are very important substances, and are of considerable value in synthetic operations. It is important to note that the sulphur atom is not directly linked to carbon, but rather through oxygen; this accounts for the ease with which the sulphuric acid residue is split off in certain reactions, *e.g.* either by heating the acid or by boiling with more alcohol in the presence of sulphuric acid.

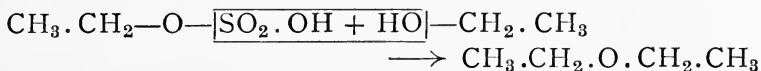
Reactions of ethylsulphuric acid and its salts.

(i) On heating it yields ethylene and sulphuric acid.

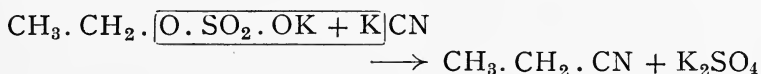


This reaction is to a certain extent reversible (see page 38).

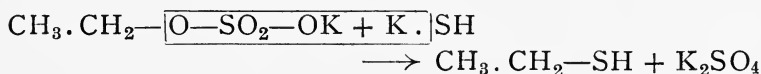
(ii) On heating with alcohol, ether is formed and sulphuric acid regenerated.



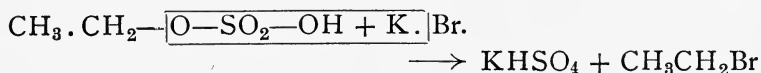
(iii) When heated with potassium cyanide a nitrile is produced.



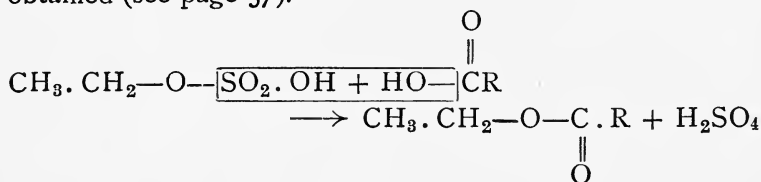
(iv) With potassium hydrogen sulphide a mercaptan or thio-alcohol is formed.



(v) On heating with potassium iodide or bromide the corresponding alkyl halide is obtained.



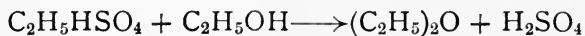
(vi) On heating with an organic acid an ethyl ester is obtained (see page 37).



PREPARATION OF DIETHYL ETHER, COMMONLY KNOWN AS ETHER.

That ethylsulphuric acid is capable of reacting with alcohol to produce diethyl ether and sulphuric acid, has been

already mentioned (see the last preparation, and also Chapter I., page 41).



In a round-bottomed flask of about half to one litre capacity 93 grams (120 c.c.) of absolute alcohol are placed, and 165 grams (88 c.c.) of concentrated commercial sulphuric acid are slowly and carefully added, the mixture being shaken after each addition.

The flask is then fitted with a cork bored with three holes. Through one of these a dropping funnel is inserted, through another a short delivery tube bent at an acute angle and leading to a well-cooled Davies condenser, while a thermometer, the bulb of which must dip *beneath the surface of the mixture*, passes through the third. The condenser is connected by means of an adapter and cork with a filter flask, the side tube of which is fitted with the customary rubber tube to carry away uncondensed ether vapour. The filter flask is cooled in ice.

The contents of the flask are then cautiously heated on the sand-bath. As soon as distillation commences more absolute alcohol is allowed to run in from the separating funnel at the same rate as the liquid distils, *i.e.* about 3 drops per second. The temperature of the liquid in the distillation flask is kept constant at about 140° . A sufficient quantity of ether will be obtained when about 200 c.c. of alcohol, exclusive of the 120 c.c. previously placed in the flask, have been run in through the dropping funnel.

The distillate, which consists principally of ether, but contains also alcohol, water and sulphurous acid, is then shaken in a separating funnel with about 5 c.c. of dilute sodium hydroxide solution. This removes sulphur dioxide and a certain amount of the alcohol. Any aldehyde which may be present is converted into aldehyde resin (see page 26).

After running off the alkaline liquid the remainder of the alcohol is removed by shaking with two successive quantities (20 c.c.) of a concentrated sodium chloride solution. Ether is less soluble in this solution than in pure water, and the loss which is bound to occur during washing is thereby diminished.

After the removal of the salt solution the still moist ether is shaken with successive small quantities of anhydrous calcium chloride, the water which separates being run off. The ether is then allowed to stand overnight in contact with anhydrous calcium chloride. Next morning it is poured off and distilled,

the usual precautions essential to manipulations in which ether is concerned being adopted. B.P. 36° .

The last traces of alcohol and moisture in the ether are extremely difficult to remove. If anhydrous "absolute" ether be required the product should be allowed to stand over sodium till all action ceases, and finally distilled over phosphorus pentoxide.

PREPARATION OF ETHYL ACETATE.

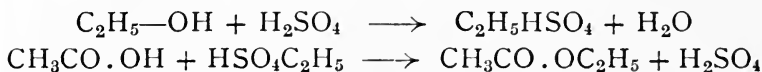
For this experiment exactly the same apparatus as that described in the last preparation is required, with the exception that the flask is heated in an oil bath rather than on a sand bath.

A mixture of 60 c.c. of concentrated sulphuric acid and 60 c.c. of absolute alcohol is placed in the flask while the tap funnel contains absolute alcohol and glacial acetic acid in equal volumes. One hundred and twenty c.c. of each can conveniently be employed.

The oil bath is then heated and the temperature of the liquid in the flask kept constant at 140° . As soon as this temperature is reached or even sooner, the contents of the tap funnel are allowed to run into the flask at the same rate as the liquid distils. When the whole has been added the distillate is transferred to a separating funnel and vigorously shaken with concentrated sodium carbonate solution to remove acetic and sulphurous acids, the treatment being continued until the upper layer, which consists of ethyl acetate, possesses an alkaline reaction. The carbonate solution is then run off. Any which remains dissolved in the ethyl acetate is removed by washing once with water. In order to remove any remaining alcohol, about 50 c.c. of a concentrated solution of calcium chloride (1 : 1) are added to the mixture which is well shaken and separated (see page 260).

Shaking with successive quantities of solid anhydrous calcium chloride then follows, after which the ester is allowed to stand overnight in contact with a few pieces of the dehydrating agent, and then distilled, using a water condenser. That fraction boiling between 74° and 79° is nearly pure ethyl acetate. Below 74° the distillate contains considerable amounts of ether, the formation of which in this reaction can readily be understood. As in the case of the preparation of ether, the process here described is to a certain extent "continuous," since sulphuric acid is regenerated, as will be

seen from the subjoined equations. After a time, however, it becomes too dilute, and the esterification ceases.



This reaction is of very general application, an enormous number of both aromatic and aliphatic acids as well as numerous alcohols coming within its scope.

Saponification of Ethyl Acetate.—Boil a few c.c. of the ethyl acetate with about three times its volume of 30 per cent. potassium hydroxide solution under an upright condenser. As soon as all oily drops have disappeared, the condenser is disconnected, and then attached in the ordinary way and the liquid distilled. Test the distillate for alcohol

- (i) by boiling a portion and applying a light to the vapour,
- (ii) by the iodoform test,
- (iii) with warm acidified potassium dichromate solution.

When no more alcohol distils as indicated by test (iii), the contents of the distillation flask are cooled and acidified with sulphuric acid and distillation continued. Acetic acid now distils, and may be recognized

- (i) by its odour,
- (ii) by neutralizing a portion of the distillate carefully with sodium hydroxide, and adding ferric chloride solution. A red coloration, changing on boiling to a red precipitate, is formed. (For equation, see page 280.)

The process of saponification is represented by the equation



CHAPTER XX

THE DESTRUCTIVE DISTILLATION OF WOOD

IF wood be heated out of contact with air (destructive distillation) it yields an inflammable gas, an aqueous distillate, and wood tar. The residue is wood charcoal.

The composition of the various products depends, of course, on the particular kind of wood employed and also largely on the temperature and the rate at which the wood is heated. Of these products the aqueous distillate (which is known as pyroligneous acid, and contains methyl alcohol, acetic acid and acetone, together with small quantities of many other substances) and the wood charcoal are the most valuable. The gas, which contains carbon monoxide, carbon dioxide, hydrogen, methane, ethylene, acetylene and higher hydrocarbons, and the tar, which consists of paraffins, phenols, etc., are often made use of in the commercial process as fuels. The so-called "Stockholm Tar," obtained principally from pine wood, is, however, of great value in preserving wood, etc.

The commercial importance of methyl alcohol, acetone and acetic acid is sufficient to justify the inclusion of an account of the destructive distillation of wood in this book, although these substances are not ordinarily used as fuels. The crude methyl alcohol obtained in this process is known as *wood spirit*, and, as mentioned on page 266, this substance is extensively used as a denaturant for alcohol. Methyl alcohol is also used in the manufacture of certain dyes, for the preparation of formaldehyde, and as a solvent in the preparation of varnishes. Acetic acid is chiefly used in the coal-tar colour manufacture, and for the preparation of acetates, which are used as pigments and as mordants in dyeing.

The amounts of these substances present in the pyroligneous acid is as follows :—

Methyl alcohol, 1 to 3 per cent.

Acetone, 0·1 to 0·5 per cent.

Acetic acid, 7 to 10 per cent.

The methyl alcohol and acetone are easily separated from the acetic acid by converting the latter into calcium acetate, and along with other substances constitute the wood spirit.

In order to illustrate the destructive distillation of wood, the retort, Fig. 35, page 188, used in the distillation of shale, is filled with strips of wood about 16 inches long and one quarter inch square section, the weight of wood taken for an experiment being noted. The receiver B is cooled in water, and to the exit tube of this receiver a water condenser is attached instead of the wash bottle C. A filter flask is connected by means of a cork to the lower end of the condenser, and from the exit tube of this flask a rubber tube is attached for conducting away the gases.

The retort is slowly heated and soon drops of liquid are seen to fall from the iron exit tube. The heating is gradually increased until finally the retort is at a dull red heat.

(The retort described on page 188 holds about 400 grams of a soft wood such as deal, cut in strips as above. This gives about 150 c.c. of distillate (pyroligneous acid and tar). Further quantities of wood should be distilled until at least half a litre of pyroligneous acid has been obtained.)

Wood Spirit.—The distillates are united and allowed to stand for some time to allow the tar to settle. The dark-coloured liquid is then poured off from the tar, filtered and distilled, using a water condenser, until nearly all has passed over.

This operation serves to free it as far as possible from the tar, but it will be obvious that a certain amount of acetic acid does not distil over and will therefore be lost.

The filtered distillate is then neutralized by the gradual addition of *milk of lime*, made by grinding up powdered lime into a thin paste with water. The acetic acid is thus converted into calcium acetate.



During the addition of the milk of lime drops of the liquid are removed periodically by means of a glass rod and placed on litmus paper. If the liquid is dark in colour, owing to the presence of tar, it is impossible to see the colour of the litmus paper at once, but after washing with water the colour is apparent. As soon as the liquid ceases to show an acid reaction the addition of milk of lime is discontinued.

The liquid is then distilled, using a fractionating column, that portion which comes over below 85° and which contains methyl alcohol (B.P. 66°), acetone (B.P. 56°), etc., being

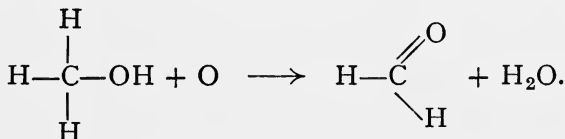
collected. This constitutes the wood spirit. The calcium acetate remains behind in solution.

(Pure methyl alcohol is obtained from wood spirit by careful fractionation in presence of milk of lime and the resulting methyl alcohol purified by conversion into dimethyl-oxalate, M.P. 54° , and subsequent hydrolysis.)

It will be noticed that the distillate possesses the characteristic smell of certain varieties of "methylated spirits," *i.e.* those which contain wood spirit as a denaturant.

On applying a light to a few drops of the liquid placed in a porcelain dish it will be found to burn.

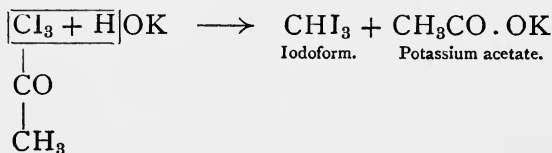
If a red-hot platinum wire be introduced into the mouth of a test-tube which contains a small quantity of the liquid which has been previously boiled, it is found that the wire continues to glow, owing to the catalytic oxidation of the methyl alcohol to formaldehyde.



(The same phenomenon is also shown in the catalytic oxidation of ethyl alcohol.)

The presence of acetone in the crude wood spirit may be shown by means of the iodoform test * as follows:—

To a portion of the liquid a few drops of a solution of iodine in potassium iodide are added. Potassium hydroxide solution is then added until the dark colour of the iodine is removed. A slight yellow precipitate indicates the presence of iodoform. Probably owing to the strong smell of the wood spirit, the characteristic smell of iodoform will be obscured. The reactions on which the production of iodoform depends are as follows:—



In some cases a precipitate of aldehyde resin is obtained on adding potassium hydroxide without the addition of iodine.

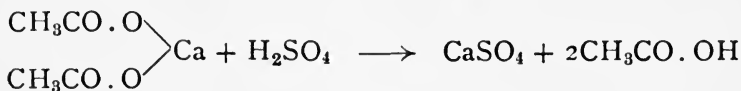
* See also page 265.

The liquid which remains in the flask after the removal of the wood spirit by distillation, and which contains calcium acetate, is filtered and evaporated to dryness in a porcelain basin, by heating first on a wire gauze and finally on the water bath. The viscous mass remaining behind, consisting of impure calcium acetate, is heated to 200° in an air oven in order to get rid of volatile matter. It is then removed from the porcelain basin and divided into two portions, one of which is to be used for the preparation of acetone and the other for the preparation of acetic acid.

Acetone.—For the preparation of acetone the calcium acetate is heated in a round-bottomed flask supported horizontally and to which a water condenser is attached as in the preparation of benzene, Fig. 38, page 201. The liquid which collects is impure acetone. It may be purified by the addition of an equal volume of water, in which acetone is soluble, and after filtering it is separated from the water by repeated distillation, using a fractionating column. The distillate is dried over calcium chloride and again distilled (B.P. 56°). Acetone is detected by its characteristic smell and the formation of iodoform with iodine in presence of potassium hydroxide. With a saturated solution of sodium bisulphite it gives a crystalline precipitate of acetone sodium bisulphite, $(\text{CH}_3)_2\text{CO} \cdot \text{NaHSO}_3$, from which acetone may be obtained quite pure on distillation with sodium carbonate solution.

Acetic Acid.—For the preparation of acetic acid the remaining portion of the crude calcium acetate is placed in a distilling flask to which a water condenser is attached, covered with concentrated commercial sulphuric acid and gently heated, the operation being carried out in a draught cupboard. The liquid which distils over below 150° is collected. The presence of acetic acid is denoted by its characteristic smell.

Its formation is represented as follows:—



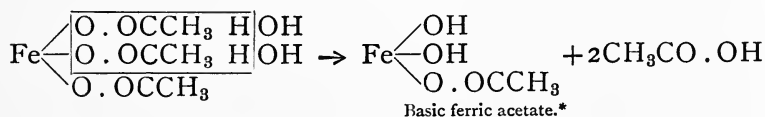
The crude acetic acid is redistilled and eventually glacial acetic acid (B.P. 118°) commences to distil. This portion of the distillate should solidify on cooling (M.P. 17°).

The acid may be recognized by means of the following reactions.

To a portion of the distillate add some alcohol and

concentrated sulphuric acid. On warming, the characteristic fruity smell of ethyl acetate is produced (see page 274).

Some of the acid is poured into water and made exactly neutral by the addition of ammonium hydroxide. Ferric chloride solution is added and a deep red-brown colour is produced owing to the formation of ferric acetate. On boiling the solution basic ferric acetate is precipitated.



It will be recalled that this reaction is made use of in qualitative inorganic analysis in removing excess of iron in a phosphate separation.

For further information regarding the destructive distillation of wood, the student is referred to Thorpe's "Dictionary of Applied Chemistry," and to "Industrial Chemistry, Organic," G. Martin (Crosby Lockwood and Son).

* The formula for this substance is often written $\text{Fe}(\text{CH}_3\text{COO})_3 \cdot \text{Fe}_2\text{O}_3$,
i.e. $3\text{Fe}(\text{OH})_2(\text{CH}_3\text{COO}) \longrightarrow \text{Fe}(\text{CH}_3\text{COO})_3 \cdot \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$.

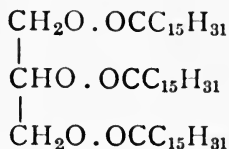
CHAPTER XXI

SAPONIFIABLE OILS

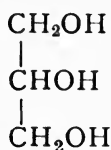
SUBSTANCES which are usually described as oils may be divided into two main classes, namely, those which are unsaponifiable, of which the petroleum oils are examples, and those which can be saponified. The latter class includes well-known substances such as olive, linseed, cotton-seed and palm oils. Paraffin wax consists of paraffin hydrocarbons of high molecular weight, but other waxes such as bees'-wax are saponifiable substances.

The members of this class of substances which are of most importance from a commercial standpoint, are those which give glycerol on saponification, that is, they are glycerol esters or *glycerides*. With the exception of petroleum or coal tar products practically all the important oils and fats are included among the latter substances. It is on account of the technical importance of these bodies as lubricants, and their use for other purposes, that a consideration of their properties has been deemed necessary.

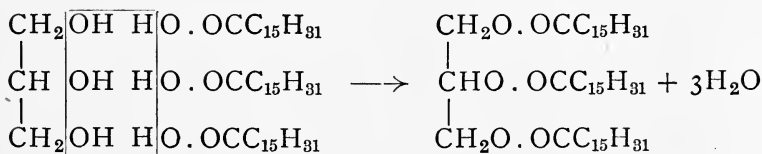
One of the principal constituents of palm and cotton-seed oils is the solid glyceride tripalmitin.



This substance may be regarded as derived from glycerol



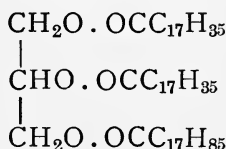
and palmitic acid $\text{C}_{15}\text{H}_{31}\text{COOH}$ as follows :—



Just as aluminium chloride is derived from aluminium hydroxide and hydrochloric acid.



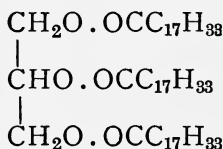
The solid glyceride tristearin *



derived from stearic acid $\text{C}_{17}\text{H}_{35} \cdot \text{COOH}$ is also an important constituent of oils and fats.

It will be noticed that the glycerides tripalmitin and tristearin are derived from saturated acids of the fatty series of the general formula $\text{C}_n\text{H}_{2n+1}\text{CO} \cdot \text{OH}$.

On the other hand, the liquid glyceride triolein,

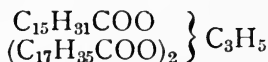


is derived from the unsaturated acid $\text{C}_{17}\text{H}_{33}\text{COOH}$ (oleic acid). This glyceride is the principal constituent of olive oil. Many natural oils and fats are mixtures in varying proportions of the three glycerides mentioned above, together with smaller quantities of other substances.

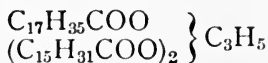
Tripalmitin, tristearin, and triolein are examples of what are known as *simple* glycerides, that is, the three hydroxyl groups of the glycerol are replaced by the same acid radical.

* It is important to distinguish between the words "stearin" which denotes a glyceride and "stearine" used in commerce to denote a certain make of candles, which, however, do not contain stearin but free stearic and palmitic acids, together with some paraffin or other wax to prevent the candles from becoming crystalline.

Glycerides are known, however, in which this is not the case, for example, the *mixed* glycerides palmitodistearin



and steardipalmitin

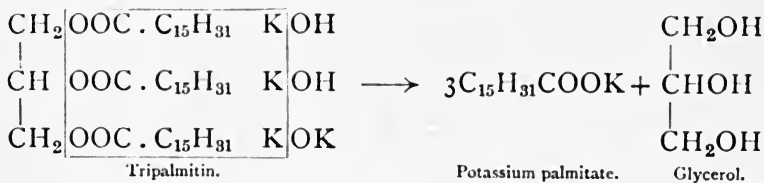


are known to occur in tallow.

A very important glyceride of lower molecular weight than those mentioned above is tributyrin, derived from butyric acid, $\text{C}_4\text{H}_9\text{COOH}$. This fat is present in butter, whilst the butter-substitute margarine contains principally glycerides of higher molecular weight.

Saponification.—The saponification of these glycerides is extremely important, and, as mentioned on page 40, this is the process which underlies the whole soap industry. Since these glycerol esters differ in molecular weights it will be obvious that different weights of alkali will be required for the saponification of a given weight of the various oils, fats, and waxes.

Thus the saponification of tripalmitin, by means of potassium hydroxide, is represented as follows:—



that is, 806 grams of tripalmitin require $3 \times 56 = 168$ grams of potassium hydroxide, or one gram of tripalmitin requires 0.208 gram or 208 milligrams of potassium hydroxide for saponification.

In a similar manner it may be calculated that for the saponification of one gram of tributyrin 485 milligrams of potassium hydroxide is required.

The determination of the amount of potassium hydroxide required for the saponification of 1 gram of the various oils is extremely important. This amount of potassium hydroxide,

expressed as milligrams, represents what is called the *saponification value* of the substance. In the following table the saponification values for various oils are given :—

<i>Oil.</i>	<i>Saponification value.</i>
Castor	183—186
Cocanut	246—260
Cotton-seed	193—195
Linseed	190—195
Olive	185—196
Palm	196—205
Rape	170—179
Whale	188—194

The presence of mineral oil, even in small quantity, in one of these animal or vegetable oils is often detected by the low figure obtained for the saponification value.

The actual determination of the saponification value of an oil or fat is carried out by Kaettstörfer's method, the principle of which is as follows :—

A known weight of the oil is heated with a measured volume of a standard solution of alcoholic potash, until saponification is complete. The excess of potassium hydroxide remaining in the solution is then determined, by titration with a standard solution of an acid. The amount of potassium hydroxide used for the saponification is thus obtained, and from this the amount of the alkali required for the saponification of one gram of the oil may be calculated.

DETERMINATION OF THE SAPONIFICATION VALUE OF A SPECIMEN OF OLIVE OIL.

Weigh out on a rough balance approximately eight grams of potassium hydroxide, which has been purified by crystallization from alcohol. Dissolve this in not more than 10 c.c. of water and add 250 c.c. of alcohol or purified methylated spirits. Mix thoroughly by warming slightly and shaking. Allow to stand for half an hour in a flask fitted with a rubber stopper. Filter quickly, if any sediment has formed, through a fluted filter, and place the solution in a bottle closed by a rubber stopper. The solution should possess only a light yellow colour if the alcohol employed was sufficiently pure.

Weigh out from 2 to 2.5 grams of the oil as follows :—

Place a small quantity of the oil in a small lipped beaker containing a short glass rod. Weigh accurately the beaker

+ rod + oil. Pour out some of the oil, about 2 to 2.5 grams, into a thick-walled glass bottle, making use of the glass rod to prevent oil running down the outside of the beaker. Re-weigh the beaker, rod, and oil, and so obtain the weight of oil transferred to the bottle. 25 c.c. of the solution of alcoholic potash measured by means of a pipette should then be added to this weighed quantity of oil and the bottle closed by means of a rubber stopper, which is securely tied in by means of string. Suspend the bottle in a water bath so that it is rather more than half immersed in the water. Heat the water to boiling, shaking the bottle frequently, and allow it to remain in the boiling water until ten minutes after all the oil has disappeared. When this is the case remove the bottle from the water bath and allow it to cool.

While this saponification is proceeding, the solution of alcoholic potash should be standardized by means of a semi-normal solution of hydrochloric acid.

As a preliminary experiment measure out 5 c.c. of the alcoholic potash, add one drop of phenolphthaleïn, and titrate with the N/2 hydrochloric acid. This gives an idea of the amount of the acid which will be required for 25 c.c. of the potassium hydroxide solution.

Repeat the experiment twice, using 25 c.c. of the alcoholic potash and ten drops of the indicator, and take the mean of the two readings. Express the result as follows :

Blank experiment 25 c.c. alcoholic potash = c.c. N/2 HCl.

When the bottle containing the saponified oil is cool the rubber stopper is removed and ten drops of phenolphthaleïn solution added. The excess of potassium hydroxide remaining in the solution is then titrated with the semi-normal hydrochloric acid. The volume of the acid required, subtracted from that required for 25 c.c. of the potassium hydroxide solution in the blank experiment, gives the volume of semi-normal hydrochloric acid corresponding to the potassium hydroxide required for the saponification.

From the equation—



it will be seen that 56 grams of potassium hydroxide are neutralized by 36.5 grams of hydrogen chloride or by 1 litre of normal hydrochloric acid.

Hence 1 litre of N/2 HCl is equivalent to 28 grams KOH.

∴ 1 c.c. N/2 HCl is equivalent to 28 milligrams of potassium hydroxide.

Therefore the weight of potassium hydroxide required for the saponification of a known weight of the oil is found, and from this the saponification value, the number of milligrams of potassium hydroxide required for the saponification of one gram of the oil, may be calculated.

Suppose that in a particular estimation—

$$\begin{array}{rcl} \text{Weight of beaker + rod + oil} & = & 32.702 \text{ grams} \\ \text{" " " part of oil} & = & 30.213 \text{ " } \\ \text{Weight of oil taken} & = & 2.489 \text{ " } \end{array}$$

Preliminary experiment—

$$\begin{array}{rcl} 5 \text{ c.c. of alcoholic potash + 10 drops phenolphthalein required} & & 5.2 \text{ c.c. N/2 HCl} \\ 25 \text{ c.c. of alcoholic potash + 10 drops " (i) } & & 25.5 \text{ c.c. N/2 HCl} \\ & & \text{(ii) } 25.4 \text{ c.c. N/2 HCl} \\ \text{Mean} & & 25.45 \text{ " " } \end{array}$$

25 c.c. alcoholic potash + oil, after saponification, + ten drops phenolphthalein required 8.0 c.c. N/2 HCl.

N/2 HCl equivalent to KOH used in the saponification

$$\begin{aligned} &= 25.45 - 8.0 \\ &= 17.45 \text{ c.c. ;} \end{aligned}$$

But 1 c.c. N/2 HCl is equivalent to 28 milligrams KOH

$$\therefore 17.45 \text{ " " } 28 \times 17.45 = 488.6 \text{ mg. KOH}$$

\therefore KOH required by 2.489 grams of oil = 488.6 milligrams,

$$\text{or 1 gram of oil requires } \frac{488.6}{2.489} = 192 \text{ milligrams KOH.}$$

Saponification value of the given oil = 192

It is obviously not essential that the hydrochloric used should be exactly semi-normal, provided its exact strength be known. For example, if the hydrochloric acid used above were 1.12 N/2 instead of exactly semi-normal, 1 c.c. of this acid would = 28×1.12 milligrams KOH.

Instead of using a stoppered bottle, the saponification may be carried out, if preferred, in a conical flask fitted with a reflux water condenser and heated on a wire gauze over a Bunsen burner. In this case the 25 c.c. of the alcoholic potash used for the blank experiment should be similarly treated on account of the absorption of carbon dioxide from the air, which affects the phenolphthalein indicator.

As mentioned on page 284, the presence of mineral oil in a saponifiable oil may be detected by the low saponification value of the latter. If a heavy mineral oil is present in appreciable quantity it may also be estimated as follows:—

A given weight of the oil, say 10 grams, is heated in a conical flask fitted with a reflux water condenser with 10 c.c. of fifty per cent. aqueous potassium hydroxide and 50 c.c. of alcohol. The mixture is boiled gently for about half an hour, and on cooling is transferred to a separating funnel. It is extracted twice with light petroleum (B.P. below 80°). This removes the heavy mineral oil from the soap solution. The petroleum solution is washed twice with fifty per cent. aqueous alcohol to remove traces of soap, transferred to a dry weighed flask, and the light petroleum distilled off.* The flask and contents are dried in the steam oven and weighed when cold. From the increase in weight the percentage of heavy mineral oil in the sample may be calculated.

In some cases, instead of estimating the amount of potassium hydroxide required for the decomposition of a fat, the mixture after saponification is treated with sulphuric acid, whereby the soaps are decomposed with the liberation of the corresponding acids. Thus, in the detection of foreign fats in butter a weighed quantity of butter-fat is saponified, and the mixture distilled with dilute sulphuric acid in a standard (Reichert-Wollny) distillation apparatus. Fatty acids of low molecular weight, such as butyric acid, are volatile in steam and soluble in water; whereas those of high molecular weight, such as palmitic and stearic acids, are only slightly volatile in steam and practically insoluble in water.

From the amount of standard alkali required to neutralize the filtered distillate it is possible, therefore, to determine the nature of the fat saponified.

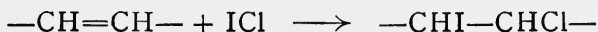
DRYING AND NON-DRYING OILS. IODINE VALUE.

One of the most important considerations in connexion with an oil is whether or not it will harden on exposure to air. Thus it is essential, for example, that a lubricating oil shall not dry on exposure to air; but, on the other hand, it is necessary that an oil used in the manufacture of paint shall harden when so exposed. Amongst the saponifiable oils, in general those derived from unsaturated acids will dry on exposure to air owing to absorption of oxygen, this absorption of oxygen taking place at the point of unsaturation of the molecule.

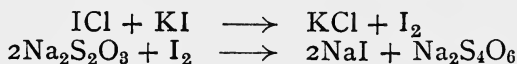
* See Fig. 40, page 206.

As is well known, unsaturated substances form compounds with halogens by direct addition, and this reaction between an oil, containing an unsaturated glyceride, and iodine is employed in the determination of what is known as the *iodine value* of an oil. This represents the percentage proportion of iodine absorbed by the oil, or the number of grams of iodine absorbed by one hundred grams of the oil. In general the higher the iodine value of an oil the more readily will it dry on exposure to air.

In the original process for the determination of the iodine value of an oil, known as Hübl's process, the oil was treated with an alcoholic solution of iodine containing mercuric chloride. In Wij's modification of the process, iodine monochloride, ICl , is employed instead of free iodine, as the time required for complete saturation with this reagent is considerably less than with free iodine. The reaction is represented as follows:—



In the actual determination a weighed quantity of the oil, dissolved in carbon tetrachloride, is treated with a measured volume of iodine monochloride solution. The mixture is allowed to stand for a certain time and the excess of iodine monochloride then estimated, after the addition of potassium iodide, by means of a standard solution of sodium thio-sulphate. The reactions which take place are as follows:—



It is essential that at least half the iodine monochloride originally present should remain in the solution after the absorption by the oil has taken place. This ensures that excess of the reagent is in contact with the oil throughout the absorption. On this account only a very small quantity of a drying oil should be used for the experiment.

From the difference in volume of thiosulphate solution required for a certain volume of iodine monochloride solution, in a blank experiment, and that required for the same volume of iodine monochloride solution after treatment with the oil, the amount of iodine absorbed by the given weight of oil is found, and hence its iodine value may be calculated. In reality, as pointed out above, it is iodine monochloride and not iodine which is absorbed by the oil; this does not affect the amount of thiosulphate required in either the blank

or test experiment, since one molecule of iodine monochloride with potassium iodide gives one molecule of iodine.

The various solutions required for the determination of the iodine value of an oil are prepared as follows:—

Decinormal sodium thiosulphate solution, 25 grams of the crystallized salt $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per litre, see Chapter X, page 177.

Starch solution prepared as described on page 178.

Potassium iodide solution.—A solution containing 10 grams of the salt per 100 c.c. of water is required.

Wij's iodine monochloride solution.—3.2 grams of finely-powdered iodine are dissolved in acetic acid (98–99 per cent.) and the solution diluted with the same solvent to 250 c.c. in a graduated flask.

5 c.c. of the solution are then treated with about 3 c.c. of 10 per cent. potassium iodide solution and 30 c.c. of water. The decinormal sodium thiosulphate solution is then run in from a burette until the colour of the iodine is practically removed. A few drops of starch solution are then added and the sodium thiosulphate run in drop by drop until the blue colour is discharged. The amount of sodium thiosulphate solution required is noted.

Pure dry chlorine is then passed into the iodine solution until the colour of the solution is changed from brown to red and until 5 c.c. of the solution, treated as before, requires twice as much sodium thiosulphate to remove the iodine as when first prepared.

The pure dry chlorine is prepared by dropping concentrated commercial hydrochloric acid on to solid potassium permanganate, the gas being passed through wash bottles containing (a) water to remove hydrochloric acid, (b) sulphuric acid to remove aqueous vapour, before being passed into the iodine solution.

The iodine monochloride solution may, if preferred, be made up by dissolving a weighed quantity of iodine trichloride in glacial acetic acid and adding sufficient iodine to convert the trichloride into monochloride.

Suppose that in a particular experiment—

$$\begin{array}{rcl} \text{Weight of beaker + rod + oil} & = & 29.685 \text{ grams} \\ \text{“ “ “ + part of oil} & = & 29.525 \text{ “} \\ \hline \text{weight of oil taken} & = & 0.160 \text{ “} \end{array}$$

This weighed quantity of oil, which was placed in a dry glass-stoppered bottle of about 300 c.c. capacity, was treated

with 10 c.c. of carbon tetrachloride, and 25 c.c. of the iodine monochloride solution. (The object of the carbon tetrachloride is to act as a solvent for the oil.) The bottle was then tightly stoppered, the stopper having been previously moistened with potassium iodide solution to prevent loss of iodine, and the mixture allowed to stand for one hour.

Blank Experiment.—25 c.c. iodine monochloride + 15 c.c. 10 per cent. KI solution + 150 c.c. water + a few drops of starch solution, required for removal of the iodine—

(i) 49.6 c.c. N/10 $\text{Na}_2\text{S}_2\text{O}_3$

(ii) 49.6 c.c. „ „

(Note.—The starch is not added until the colour of the iodine is practically discharged.)

The iodine monochloride solution which has been in contact with the oil was then treated in the same bottle with potassium iodide solution, water and starch solution as in the blank experiment, and sodium thiosulphate solution run in.

Volume of N/10 thiosulphate required = 26.8 c.c.

Amount of iodine monochloride absorbed by the oil is thus equivalent to

$$49.6 - 26.8 = 22.8 \text{ c.c. N/10 } \text{Na}_2\text{S}_2\text{O}_3$$

but 1 c.c. N/10 $\text{Na}_2\text{S}_2\text{O}_3$ = 0.0127 gram iodine.

\therefore 22.8 c.c. „ „ = $0.0127 \times 22.8 = 0.2896$ gram iodine.

This iodine is equivalent to the iodine monochloride absorbed by the oil.

\therefore 0.16 gram of the oil would absorb 0.2896 gram iodine, or 100 grams would absorb $\frac{0.2896}{0.16} \times 100 = 181$ grams iodine, or iodine value of the oil = 181.

The iodine values for various oils are given in the table below. Those which have iodine values above 120 are usually called *drying* oils, those of which the iodine value is between 95 and 120 *semi-drying* oils and those having an iodine value less than 95, are known as *non-drying* oils.

Oil.	Iodine value.
Castor	85-95
Cocoonut	8-10
Cotton-seed	104-110
Linseed	175-200
Olive	80-86
Palm	52-57
Rape	95-100
Whale	110-146

As a general rule glycerides of unsaturated acids have comparatively low melting points, that is, oils and fats having high iodine values often possess a softer consistency than those having low iodine values. The hardening and deodorizing of oils and fats by the conversion of unsaturated into saturated glycerides, which is becoming of great technical importance, has been referred to in the Chapter on Hydrogenation.

For further information on the subject of saponifiable oils the student is referred to the following books :—

“The Chemical Technology and Analysis of Oils, Fats and Waxes,” by J. Lewkowitsch. (Macmillan & Co.)

“The Laboratory Companion to Fats and Oil Industries,” by J. Lewkowitsch. (Macmillan & Co.)

“Commercial Organic Analysis,” Vol. II., by Allen. (J. and A. Churchill.)

CHAPTER XXII

THERMOCHEMISTRY

THEORETICAL.

THIS important subject deals with the relation which exists between the chemical energy of a system, which is a form of potential energy, and its heat or thermal energy.

In the majority of chemical reactions heat is evolved, and this is denoted by an equation such as



which means that when 12 grams of carbon (charcoal) unites with 32 grams of oxygen to produce 44 grams of carbon dioxide 97,000 units of heat are evolved ; or the "system" composed of 12 grams of free carbon and 32 grams of free oxygen, possesses 97,000 calories more energy than the 44 grams of carbon dioxide produced by their combination.

This unit of heat, *the calorie*, is the amount of heat required to raise the temperature of one gram of water one degree Centigrade (from 4° C. to 5° C.). It is inconveniently small for practical purposes, and on this account the *kilogram-calorie*, denoted Cal., is more frequently employed. This unit of heat represents the amount of heat required to raise the temperature of one kilogram of water one degree Centigrade, and is obviously one thousand times as great as the previous unit, the calorie.

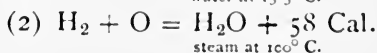
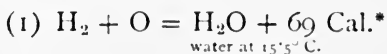
The British Thermal Unit will be considered later.

From the fact that free carbon and free oxygen possess much more energy than the carbon dioxide produced by their combination, and from similar considerations, it follows that the free elements must possess a considerable amount of free energy, but what these *absolute* amounts are is quite unknown. In chemical changes, however, we have only to deal with *differences*, and not with the *absolute* amounts of energy possessed by various systems. It has been found convenient,

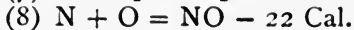
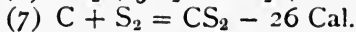
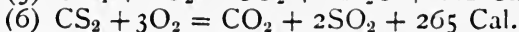
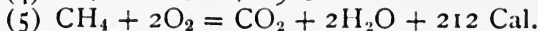
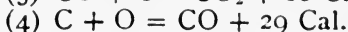
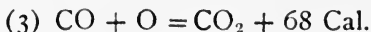
therefore, to regard the *intrinsic* energy possessed by all the elements as zero.

A chemical reaction in which heat is evolved is said to be *exothermic*, and a substance produced from its elements with the evolution of heat, is said to be an *exothermic* substance. On the other hand, if heat is absorbed in a chemical reaction, the reaction is said to be *endothermic*, and a substance produced from its elements with absorption of heat is said to be an *endothermic* substance.

Thermochemical Equations.—Some typical thermochemical equations are given below—



The difference between these two amounts of heat is due principally to the *latent heat* of steam (that is, the heat evolved when 1 gram of steam at 100° C. is converted into water at 100° C., and is equal to 537 calories), which would account for a difference of $18 \times 537 \text{ calories} = 9.7 \text{ Cal.}$ If the water be allowed to cool to the ordinary temperature (60° F. = 15.5° C.) an additional amount of heat is evolved, equal to $(100 - 15.5) = 84.5 \text{ calories} = 0.0845 \text{ Cal. per gram of water produced, or for 18 grams, } 18 \times 0.0845 = 1.5 \text{ Cal.}$



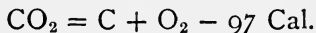
It will be noticed that it is usual to write thermochemical equations in their simplest form. In writing several of the above equations in the ordinary way it would be usual to multiply throughout by two.

Heats of Combustion and of Formation.—In the equation



* All calorific values throughout this chapter are given in *kilogram-calories*, as in general with a calorific value expressed in small calories the last two figures are without significance owing to experimental errors, and, moreover, the numbers obtained are inconveniently large.

97 Cal. is said to represent the *heat of combustion* of carbon (it refers, of course, to 12 grams or a gram-atom of carbon). This amount of heat also represents the *heat of formation* of carbon dioxide (a gram-molecule or 44 grams) from carbon (charcoal) and oxygen. From the principle of the conservation of energy it follows that the amount of *energy* required to decompose a substance must be exactly equal to the amount of energy evolved in its formation. Thus, the above equation may equally well be written—



that is, in the decomposition of 44 grams of carbon dioxide into 12 grams of carbon and 32 grams of oxygen an absorption of an amount of heat equal to 97 Cal. would take place. In general the heat of formation of a compound is numerically equivalent to its heat of decomposition, but of opposite sign.

It might be expected that the greater the heat of formation of a substance, the greater would be its stability. In many cases this is found to be the case. On the other hand, if heat is absorbed in the formation of a compound, that substance is often found to be unstable.

In the equation (3)



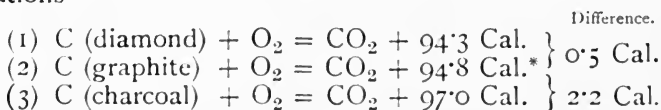
68 Cal. represents the *heat of combustion* of 28 grams (1 gram-molecule or 22.4 litres at normal temperature and pressure) of carbon monoxide.

The heat values in equations (5) and (6) represent the heats of combustion of gram-molecules of methane and carbon disulphide respectively, whilst the heat values in equations (4), (7), and (8) represent the heat of formation of one gram-molecule of carbon monoxide, carbon disulphide and nitric oxide from their respective elements.

In some of the cases mentioned above the heat values are obtained by direct experiment, but in other cases these values have to be determined indirectly, as will be shown later.

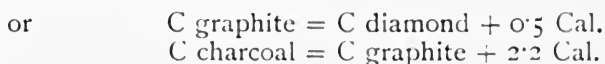
It will probably be noticed that in the various text-books dealing with this subject, different heat values are given for the same chemical reaction. These differences are not necessarily due to the non-agreement of the experimental results of various investigators, but to the fact that in some cases the equations refer to different allotropic modifications of a substance, or to the fact that a correction owing to volume changes has been made in the observed value. Thus the

heat of combustion of carbon is represented by the three equations—



Since 0.5 Cal. less heat is evolved when 12 grams of diamond are burnt to 44 grams of carbon dioxide, of which of course there is only one modification, than when an equal weight of graphite is burnt, it follows that by the conversion of 12 grams of graphite into diamond, an amount of heat equal to 0.5 Cal. would be evolved.

Similarly, in converting 12 grams of charcoal into graphite 2.2 Cal. would be evolved.



and finally by converting 12 grams of charcoal into diamond 2.7 Cal. would be evolved.

Thus although, as has been pointed out previously, the *absolute* amount of free energy possessed by the elements is quite unknown, the energy change which takes place when an element is converted into an allotropic modification may be measured indirectly.

A correction is sometimes applied in thermochemical equations for the change in volume accompanying a chemical change, thus in the reaction represented by the equation



a certain amount of work is performed against the pressure of the atmosphere by the hydrogen which is set free.

If the temperature at which the hydrogen is collected be 20° C., it can be calculated that the work performed against the atmospheric pressure is equal to 0.586 Cal.

Thus the total difference between the energy of the system before and after the solution of the zinc amounts to

$$34.2 + 0.586 = 34.786 \text{ Cal.}^\dagger$$

Calculation of Heats of Formation from Heats of Combustion.—The actual determination of the heats of formation and

* From recent experiments carried out by Roth and Wallasch (*Ber. der Deutsch. Chem. Ges.* 1913, 46, 896) it would appear that the heat of combustion of graphite is slightly *less* than that of diamond.

† Similar considerations give rise to the terms heats of combustion at *constant volume* and at *constant pressure*.

more especially of the heats of combustion of various substances is extremely important.

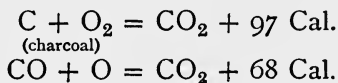
The heat of combustion of a substance is found by determining experimentally the amount of heat evolved by the complete combustion of a weighed quantity of a solid or liquid, or a measured volume of gas, the experiment being carried out in a suitable calorimeter as described later. In purely scientific work the heat of combustion refers to the amount of heat produced in the complete combustion of one gram-molecule of the substance. In commercial work the term *calorific power* is used to denote the amount of heat produced by the complete combustion of unit weight (1 gram, 1 kilogram, or 1 pound) of the fuel.

In a case such as the formation of carbon dioxide from carbon and oxygen, the heat of formation of carbon dioxide is the same as the heat of combustion of carbon, but in other cases the heat of formation of a substance must be found indirectly owing to experimental difficulties. Thus it is impossible to burn carbon with the formation of carbon monoxide *only*, and so the heat of formation of carbon monoxide cannot be determined by direct experiment.

It has been established that the heat evolved in any definite chemical change depends only on the initial and final stages, and is quite independent of intermediate stages or of the rate at which the reaction proceeds.

This law, which is known as the *law of Hess*, can be applied to determine the heat evolved in a particular reaction, which cannot be carried out directly in a calorimeter. Thus, suppose it is required to find the heat of *formation* of carbon monoxide.

From the equations



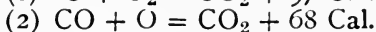
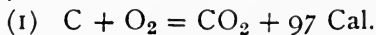
in which the heat values are determined experimentally, it will be seen that less heat, to the extent of $97 - 68 = 29$ Cal. is produced in the formation of 44 grams of carbon dioxide from carbon monoxide and oxygen than from free carbon and free oxygen.

In the latter reaction the carbon has already united with oxygen to produce carbon monoxide, and the difference in the heat values of the two equations is due to this combination

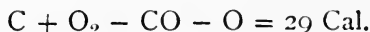
or



These thermal relations might also be considered algebraically as follows :

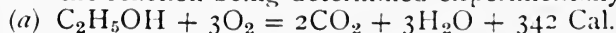


Subtracting (2) from (1) we get an equation—

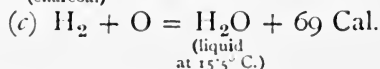
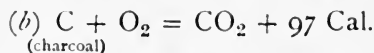


Similarly, to find the heat of formation of alcohol from its elements.

The combustion of alcohol is represented as follows ; the heat of the reaction being determined experimentally :—

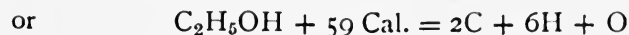


The production of carbon dioxide and water (liquid) from their elements is represented by the following equations :—



In the formation therefore of $2CO_2 + 3H_2O$ from their elements (carbon, hydrogen, and oxygen) an evolution of heat equal to $2 \times 97 + 3 \times 69 = 194 + 207 = 401$ Cal. would take place. In the formation of $2CO_2 + 3H_2O$ in the combustion of 1 gram-molecule of alcohol, equation (a), less heat, namely, 342 Cal., is evolved.

The difference between these two heat values, $401 - 342 = 59$ Cal., must therefore be the heat required to decompose 1 gram-molecule (46 grams) of alcohol into its elements.



that is, the heat of formation of alcohol from its elements would be 59 Cal.

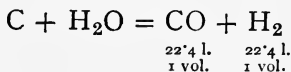
CALCULATION OF THE CALORIFIC POWERS (OR CALORIFIC VALUES) OF FUELS.*

A problem of considerable importance in thermochemistry is the calculation of the calorific power of a fuel of known composition, that is, the amount of heat produced on the combustion of a given amount of the substance.

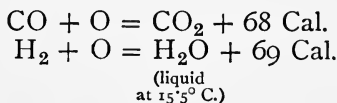
One of the simplest cases is the calculation of the calorific power of 22.4 litres of water gas at normal temperature and pressure.

* These two terms are synonymous.

Water gas being made by the action of steam on heated carbon consists *theoretically* of equal volumes of hydrogen and carbon monoxide.

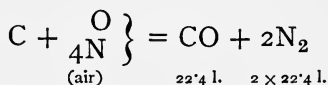


From the equations



22.4 litres of carbon monoxide + 22.4 litres of hydrogen, both at normal temperature and pressure, on combustion would yield $68 + 69 = 137$ Cal. \therefore 22.4 litres of the mixture would yield 68.5 Cal. (gross).

Similarly, producer gas consists theoretically of one volume of carbon monoxide mixed with two volumes of nitrogen, as will be seen from its formation by the action of air on heated carbon.



The nitrogen being incombustible the calorific power of 22.4 litres of this gas at normal temperature and pressure would be

$$\frac{68}{3} = 22.7 \text{ Cal.}$$

It should be noted that in calculating the calorific power of a fuel containing hydrogen or hydrocarbons, the question as to whether the heat of combustion of the hydrogen is to refer to the production of steam or water has to be considered.

Gross and Net Calorific Powers.—If it is assumed that liquid water is produced, then a greater amount of heat would be produced than if only steam were formed, as explained on page 293.

On this account the terms *gross* and *net* calorific powers are often made use of.

The gross value corresponds to the formation of liquid water.

In England it is usual to regard the products as cooled to

60° F. (15·5° C.), whereas in France the calculation is made on the assumption that water exists in the liquid state at 100° C. In Germany and Austria the calorific powers are calculated on the assumption that the water remains as steam at 100° C.

The value given above for the calorific power of water gas is thus the *gross* value.

Relation between English and Metric Thermal Units.—In connexion with commercial work in this country another heat unit is employed instead of the calorie, and it is therefore necessary to define a British Thermal Unit, denoted B.T.U. (or B.Th.U.). This unit represents the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit (from 60° F. to 61° F.).

Its relation to the calorie and Kilogram-Calorie is shown as follows :—

As previously stated, one Kilogram-Calorie (denoted Cal.) is the amount of heat required to raise the temperature of one kilogram of water 1° C.

1 kilogram = 2·2 pounds.

So that 1 Cal. would raise the temperature of 2·2 pounds of water 1° C.,

$$\text{but } 100^{\circ} \text{ C.} = 180^{\circ} \text{ F.}^* \text{ or } 1^{\circ} \text{ C.} = 1\cdot8^{\circ} \text{ F.}$$

∴ 1 Cal. would raise the temperature of 2·2 pounds of water 1·8° F. or 1 pound of water $1\cdot8 \times 2\cdot2 = 3\cdot96^{\circ} \text{ F.}$; but 1 B.T.U. raises the temperature of 1 pound of water 1° F., hence 1 Cal. (kilogram degree Centigrade) = 3·96 B.T.U. (pound degree Fahrenheit) or 1 B.T.U. = 0·253 Cal. = 253 calories.

If, however, the *calorific power* of a substance is expressed as Kilogram-Calories per kilogram, and it is required to calculate its calorific power in B.T.U. per pound, it is only necessary to multiply the Kilogram-Calories by 1·8.

For example, 1 kilogram of a substance on combustion gives out x Cal.

* Since the number of degrees between the boiling point and freezing point according to the Centigrade scale is 100 and on the Fahrenheit scale $212 - 32 = 180$, the boiling points being 100° and 212°, and the freezing points 0° and 32° respectively.

Hence, to convert temperature Fahrenheit to temperature Centigrade, subtract 32° and multiply the remainder by $\frac{100}{180}$, i.e. by $\frac{5}{9}$.

Or Temp. Centigrade = (Temp. Fahrenheit - 32) $\times \frac{5}{9}$.

$$\text{C.}^{\circ} = (\text{F.}^{\circ} - 32) \frac{5}{9} \text{ or } \text{F.}^{\circ} = \frac{9\text{C.}^{\circ}}{5} + 32$$

$$\begin{aligned} i.e. \ 2.2 \text{ pounds of the substance} & \dots \dots \dots x \text{ Cal.} \\ \therefore 1 \text{ pound} & \quad \quad \quad \text{,,} \quad \quad \quad \text{,,} \quad \dots \dots \dots \frac{x}{2.2} \text{ Cal.} \end{aligned}$$

$$\text{but } 1 \text{ Cal.} = (1.8 \times 2.2) = 3.96 \text{ B.T.U.}$$

$$\therefore \frac{x}{2.2} \text{ Cal.} = \left(\frac{1.8 \times 2.2x}{2.2} \right) = x \times 1.8 \text{ B.T.U.}$$

or 1 pound of the substance on combustion gives 1.8 times as many British Thermal Units as Kilogram-Calories given by the combustion of 1 kilogram.

Another unit of heat, the *pound degree Centigrade*, is sometimes used in this country in connexion with the calorific value of solid and liquid fuels. It denotes the amount of heat required to raise the temperature of one pound of water one degree Centigrade. Its relation to the B.T.U. is the same as that of the degree Centigrade to the degree Fahrenheit or one *pound degree Centigrade* = 1.8 B.T.U.

With gases the calorific power in this country is sometimes expressed as B.T.U. per cubic foot and sometimes as calories per cubic foot.

Further Calculations of Calorific Powers—(a) Gaseous Fuels.—Having defined the British Thermal Unit, and knowing its relation to the Calorie, we may for example calculate the calorific power of 1000 cubic feet, at normal temperature and pressure, of a sample of coal gas of known composition, and express the result in either Calories or British Thermal Units.

Suppose the gas on analysis is found to contain

Hydrogen	= 50% by volume.
Methane	= 35% „ „
Carbon monoxide	= 10% „ „
Ethylene	= 3% „ „
Nitrogen	= 2% „ „

From the heats of combustion given on pages 292, 293 and 327, it follows that on the complete combustion of 1 gram of carbon $\frac{9}{2} = 8.1$ Cal. are evolved.

Similarly the heat produced by the combustion of 1 gram of hydrogen with production of liquid water at $15.5^{\circ} \text{C.} = \frac{6.9}{2}$

		= 34.5 Cal.
from 1 gram of carbon monoxide		= 2.43 Cal.
„ „ „	„ methane	= 13.3 Cal.
	(to CO_2 and liquid water)	
„ „ „	„ ethylene	= 12.1 Cal.
	(to CO_2 and liquid water)	

The volumes of the various combustible gases in 1000 cubic feet of the mixture may be converted into litres by means of the relation 1 cubic foot = 28.3 litres.

Volume of hydrogen in the gas	$\frac{50}{100} \times 1000 \times 28.3 = 14150$ litres
" " methane	$\frac{35}{100} \times 1000 \times 28.3 = 9905$ "
" " carbon monoxide	$\frac{10}{100} \times 1000 \times 28.3 = 2830$ "
" " ethylene	$\frac{5}{100} \times 1000 \times 28.3 = 849$ "

The nitrogen, being incombustible, may be neglected in calculating the calorific power.

From the fact that the molecular weight of any gas in grams occupies 22.4 litres at normal temperature and pressure, the weight in grams of the various combustible constituents may be calculated, and hence the heat produced by their combustion.

	Volume in litres at N.T.P.	Weight in grams.	Calorific Power (for 1 gram).	Heat produced by combustion of given weight.
Hydrogen	14150	1263	34.5 Cal.	43,574 Cal.
Methane	9905	7075	13.25 "	93,744 "
Carbon monoxide . .	2830	3537	2.43 "	8,596 "
Ethylene	849	1061	12.1 "	12,838 "
Total.				158,752 Cal.

Since 1 Cal. = 3.96 B.T.U. 158,752 Cal. = 628,657 B.T.U. The heat produced by the combustion of 1000 cubic feet of the coal gas is thus 158,752 Cal. (kilogram degree Centigrade) or 628,657 B.T.U. (pound degree Fahrenheit) gross.

The problem could be simplified by calculating directly the amount of heat evolved on the combustion of the given volumes of the constituent gases, making use of the fact that the molecular heat of combustion of each gas refers to 22.4 litres at N.T.P. as in the calculation of the calorific power of water gas, etc. (page 298).

(b) **Solid Fuels.**—The values derived above for the *calorific power* (heat produced by the combustion of 1 gram) of carbon = 8.1 Cal. and for hydrogen (to liquid water) = 34.5 Cal., may be made use of in calculating the calorific power per gram of a solid fuel of known composition containing only carbon and hydrogen. It will be equal to

$$\frac{\% \text{ of carbon} \times 8.1 \text{ Cal.} + \% \text{ of hydrogen} \times 34.5 \text{ Cal.}}{100}$$

If the fuel contains oxygen it is assumed that this oxygen is used up in the combustion of some of the hydrogen, so that the amount of hydrogen remaining for combustion by means of "external" oxygen is equal to weight of hydrogen present minus $\frac{\text{weight of oxygen present}}{8}$ (since 1 gram of hydrogen unites with 8 grams of oxygen in the formation of water).

The gross calorific power per gram of such a fuel will equal—

$$\% \text{ carbon} \times 8.1 \text{ Cal.} + \left(\% \text{ hydrogen} - \frac{\% \text{ oxygen}}{8} \right) \times 34.5 \text{ Cal.}$$

100

In the majority of cases it is found that the calorific power of a complex fuel such as coal, calculated as above, is in close agreement with the observed values.

It should, however, be noted that in *calculating* the calorific power of a fuel in this manner, no allowance is made for the heats of *formation* of its constituent compounds. These values for the heats of formation are determined indirectly from the difference between the calculated and observed heats of combustion of compounds as explained on page 297, where the heat of formation of alcohol is calculated.

In the case of a complex substance, such as a coal, where the observed and calculated calorific powers are in close agreement, the heats of *formation* of the constituent substances must either be very small, or exothermic and endothermic compounds must be present in amounts which are equivalent as regards heats of formation.

In the case of liquid fuels the calculated and observed calorific powers are not as a rule in close agreement, on account of the necessity for the correction for heat of formation.

Calculation of the Temperature attained on Combustion.—Another calculation sometimes met with in connexion with this subject is that of the actual *temperature* attained by the combustion of a fuel of known calorific power.

For example, from the equation



for the combustion of one gram of carbon $\frac{32}{12}$ grams of oxygen are required, and $\frac{44}{12}$ grams of carbon dioxide are produced with evolution of an amount of heat = 8.1 Cal.

Now in any heat change the quantity of heat involved

= mass of substance heated \times its specific heat \times its rise in temperature.

The specific heat of carbon dioxide at constant pressure and for comparatively low temperatures is 0.216.

Thus quantity of heat involved 8.1 Cal. or 8100 calories
 = $\frac{4\frac{1}{2}}{12} \times 0.216 \times \text{rise of temperature}$ (where $\frac{4\frac{1}{2}}{12}$ is the weight of carbon dioxide heated and 0.216 its specific heat).

Whence the rise of temperature is approximately 10,000° C.

This is on the assumption that the combustion is carried out in oxygen without any loss of heat by radiation, etc. If the combustion were carried out in air, the temperature attained would obviously be less, since allowance must be made for the heat required to raise the temperature of the nitrogen.

Excess of air will also lead to a lowering of the temperature, and, moreover, the specific heats of gases vary with the temperature, so that it is clear that the calculation of the temperature attained in a particular reaction is a somewhat complicated matter.

Evaporative Value of Fuels.—In connexion with fuels the term *evaporative value* is often employed to denote the weight of water at 100° C. which would be converted into steam at the same temperature by the amount of heat evolved on the combustion of unit weight of the fuel. Thus if a fuel has a calorific power of 8000 Cal. per kilogram; since 537 calories (0.537 Cal.) are required to convert 1 gram of water at 100° C. into steam at the same temperature 8000 Cal. will vaporize $\frac{1 \times 8000}{0.537}$ gms. of water = 14.9 kgs.; or 1 kg. of the fuel will vaporize 14.9 kgs. of water at 100° C., *i.e.* the fuel has an evaporative value of 14.9.

THE PRACTICAL DETERMINATION OF HEATS OF COMBUSTION OR CALORIFIC POWERS OF FUELS.

The principle underlying all the methods for these determinations is exactly the same. A weighed amount of the substance is completely burned to water, carbon dioxide, etc., the combustion taking place in an apparatus known as a calorimeter and under such conditions that no carbon monoxide, unburnt vapours, etc., escape. The heat produced by the combustion is taken up by a known weight of water. From the rise in temperature of this water, which must be

determined with great accuracy, the amount of heat liberated in the combustion is found, and from this the calorific power of the fuel calculated, that is, the amount of heat produced by the complete combustion of one gram of the fuel.*

In addition to the water in the apparatus, the containing vessel, combustion chamber, thermometer, etc., are also heated, and the heat required for this purpose must also be taken into account. This gives rise to the introduction of what is known as the *water equivalent* of the calorimeter, which may be defined as the weight of water which would be heated 1°C . by the amount of heat required to raise the temperature of the whole of the apparatus in contact with the water in the calorimeter 1°C . Its value may be calculated by multiplying the mass of each part of the apparatus in contact with the water by the specific heat of the material of which it is composed and adding together the products. Thus if 200 grams of brass are in contact with the water, the specific heat of brass being 0.094, the amount of heat required to raise the temperature of this 200 grams of brass 1°C . is $200 \times 0.094 = 18.8$ calories.

Since 1 calorie is the amount of heat required to raise the temperature of 1 gram of water 1°C ., 18.8 calories would raise the temperature of 18.8 grams of water 1°C .; or the water equivalent of 200 grams of brass of specific heat 0.094 is 18.8 grams of water.

Similarly for the glass and other materials in contact with the water.

The water equivalent of a calorimeter may also be determined experimentally

(i) by placing in it a given weight of water previously heated to a known temperature and noting the fall in temperature produced;

(ii) by burning in the calorimeter a known weight of a substance of known heat of combustion.

The latter method is the one generally adopted, and is described later.

A method by which a known amount of heat is imparted

* An instrument known as the Fery Bomb Calorimeter is described in the *Journal de Physique*, 1912, p. 550. (See also *Engineering*, Sept. 20th, 1912, and *The Electrician*, Sept. 13th, 1912.) The principle of combustion employed is similar to that in other bomb calorimeters, but a thermo-electric method is employed for indicating the rise of temperature; a millivoltmeter calibrated to read in calories, or B.T.U., indicates directly the calorific value of the fuel. The use of water and of thermometers is thus dispensed with. It is claimed that the readings obtained are accurate to within 50 calories.

electrically to the apparatus has also been adopted in some cases.

In the determination of heats of combustion four classes of calorimeters are met with.

(1) Those in which the fuel is mixed with an oxidizing agent such as a mixture of potassium nitrate and chlorate, as in the Lewis Thompson apparatus; or with sodium peroxide, as in the Parr and Wild calorimeters. Such calorimeters are generally used for determinations of the calorific powers of coals and other solid fuels.

(2) Those in which the substance is burned in a stream of oxygen at atmospheric pressure, the products of combustion giving up their heat to the water in the calorimeter by either (a) bubbling through it, as in the William Thomson instrument and its modifications such as the Rosenhain and Darling calorimeters; or (b) passing into a cooling chamber in the calorimeter and finally escaping into the air, as in the Fischer apparatus.

Such instruments are usually employed for the determination of heats of combustion of solids, but with certain modifications are suitable for use with liquid fuels also.

(3) Those in which the combustion is carried out with oxygen under pressure in a closed vessel, the so-called bomb calorimeters, such as those of Berthelot and Mahler.

This kind of apparatus is universally regarded as the most reliable for determining the heats of combustion of solids and liquids, and is the one generally employed for accurate work, since with it combustion is more complete than with any other kind of apparatus. It is also possible to use it for determining the calorific values of gases, but these are more usually determined by employing a so-called gas calorimeter.

(4) Those in which a measured volume of gaseous fuel is burned in an apparatus through which a stream of water is continually passing. From the difference in temperature between the water at the inlet and the outlet, and the volume of water passed through the calorimeter, the amount of heat produced by the combustion of the gas is found. Examples of such instruments are met with in the Junker and Boys gas calorimeters.

With certain modifications these instruments are also suitable for determining the calorific powers of light oils by the combustion of a mixture of the oil vapour and air (see paper by Watson, *Journ. Royal Soc. Arts*, 1910, 58, 990).

Of these various instruments it is proposed to deal fully

with only the William Thomson, Rosenhain and the Mahler bomb calorimeters.*

The William Thomson Calorimeter.—This apparatus (Fig. 43) consists of a glass combustion chamber, which fits on to a brass base by means of springs, and contains a platinum crucible in which the fuel to be burned is placed.

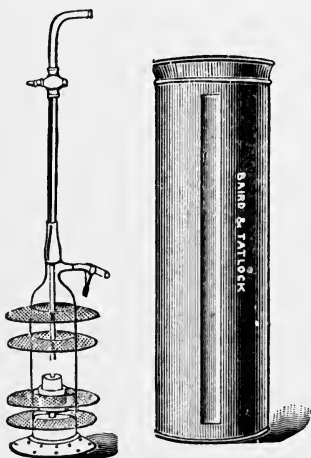


FIG. 43.—William Thomson calorimeter.

Oxygen is passed in through the vertical tube, and the products of combustion and excess of oxygen escape through the holes in the brass support at the foot of the chamber.

The combustion chamber is surrounded by wire gauze baffle discs, which serve to break up the escaping gases into small bubbles, and thereby cause them to give up their heat entirely to the water.

This part of the apparatus is immersed in a measured amount of water at a known temperature, contained in a narrow, tall glass beaker, which is surrounded by a metal vessel fitted with a glass slip, through which the progress of the combustion may be watched.

The combustion of the fuel is started by means of a small fuse, prepared by steeping a strand of cotton wick in a solution of potassium nitrate and afterwards drying it.

The rise in temperature is observed by means of a thermometer graduated in tenths of a degree.

In the determination, 1 gram of the fuel, preferably in the form of a pellet,† is weighed accurately with the platinum crucible, which is then placed in its pipe-clay support.

2000 c.c. of water, taken from a supply which has stood for some time in the room where the determination is to be made, are then placed in the large beaker, and the temperature of the water accurately noted after being thoroughly stirred.

The thermometer should be suspended so that its bulb is about 5 cms. below the surface of the water.

* For a description of the various calorimeters mentioned above, and for a comparison of the results obtained with these instruments, see Brame's "Fuel" (Arnold), pp. 317-340.

† If the sample be in the form of a powder some of it may be thrown out of the crucible by the escape of volatile products.

An oxygen cylinder should be attached to a large wash bottle containing water by means of pressure tubing, and the exit tube of this wash bottle attached to the brass inlet tube of the combustion chamber. The use of the wash bottle ensures that the oxygen supplied for combustion is saturated with water vapour. With dry oxygen the combustion is not so complete, and heat would be absorbed from the water in the calorimeter by the evaporation caused by bubbling dry oxygen through it.

In order to ensure that the oxygen is at the same temperature as the apparatus, it should be passed through a large coil of flexible metal tubing before passing into the wash bottle.

The oxygen inlet tube should be raised at first so that its end is near the top of the chamber. A fuse of the prepared wick about 2.5 cms. long is then placed upright in the crucible and ignited. The combustion chamber is at once placed over the crucible, and the whole transferred to the beaker and immersed in the water, a gentle stream of oxygen being passed through the apparatus. The amount of oxygen supplied is regulated so that the combustion does not become too violent. When the combustion is nearly complete the oxygen tube is lowered until its end is only slightly above the crucible.

When the combustion is at an end the oxygen supply is cut off and the combustion chamber raised so that the clip on the rubber tube attached to the side tube may be opened. On again lowering the apparatus into the water the gases from the combustion chamber will be driven out through this side tube, and water will come into contact with all parts of the apparatus which have been heated.

The contents of the beaker are then thoroughly mixed by raising and lowering the combustion chamber, and the maximum temperature registered by the thermometer is noted. The time over which the combustion extends should also be noted. (See radiation correction, next page.)

In order to complete the calculation it is necessary to find the water equivalent of the calorimeter. This is determined in a separate experiment by employing a given weight of a substance of known calorific value. Thus, if 1 gram of a sample of a standard coal, or of some other standard substance, is known to give 8500 calories on combustion, and the rise of temperature observed with 2000 grams of water in the calorimeter is 3.8°C. , then if x = the water equivalent of the calorimeter, the 8500 calories is taken up by $2000 + x$ grams of water whereby the temperature is raised 3.8°C.

Amount of heat = mass of water heated \times rise of temperature,

$$\begin{aligned}\therefore 8500 &= (2000 + x)3.8 \\ \text{whence } 3.8x &= 900 \\ \therefore x &= 237\end{aligned}$$

That is, the water equivalent of the calorimeter is 237 grams ; or, 8500 calories will heat 2237 grams of water 3.8° C.

2000 grams of water were employed,

\therefore water equivalent of calorimeter = 237 grams of water.

In the determination described above, no notice is taken of the fact that heat will be lost from the calorimeter during the combustion by radiation, etc., whilst the temperature of the water is rising to its maximum value. This loss may be allowed for as follows, the correction being known as the radiation correction.

After the maximum temperature is reached the apparatus is allowed to cool for a period of time equal to half that taken for the combustion, a slow stream of oxygen being passed through the apparatus meanwhile, the clip on the side tube being closed.

The fall of temperature noted during this period is added to the observed rise as the radiation correction.

Having found the water equivalent of the calorimeter and the radiation correction, we have all the data necessary for finding the calorific power of the given fuel.

Amount of heat evolved, in calories, by the combustion of a given weight of fuel

$$\begin{aligned}&= (\text{Mass of water in calorimeter} + \text{water equivalent}) \\ &\times (\text{rise of temperature} + \text{radiation correction}).\end{aligned}$$

From this the amount of heat evolved by the combustion of 1 gram of the fuel in calories, or 1 kilogram in Kilogram-Calories, or 1 pound in British Thermal Units may be calculated.

The Rosenhain Calorimeter.—This calorimeter (Fig. 44) is a modified form of the W. Thomson instrument. It differs from the latter in having an electric ignition, which is produced by passing a current through a short length of platinum wire. It is so arranged that this ignition device can be drawn out of contact with the fuel after combustion has started, otherwise it would be damaged in the course of the combustion and eventually destroyed.

The combustion chamber consists of an ordinary incandescent lamp chimney closed at the ends by brass plates, the junctions being made gas-tight by means of rubber

washers. The gases from the combustion chamber pass through a ball valve, which prevents the water from entering. When it is necessary to allow the water to enter, the ball can be raised by means of the lever and the outlet tap at the top of the chamber opened.

For the determination of the calorific power of a coal by means of this instrument, a weighed quantity of the substance (about 1 gram) in the form of a pellet is placed on a silica tray in the combustion chamber and the brass plates screwed together, care being taken not to screw too tightly.

The ignition wire is then placed in contact with the pellet. 2500 c.c. of water at the laboratory temperature are next introduced into the calorimeter vessel, and the latter placed in the wooden case. The combustion chamber is then lowered into the calorimeter, the thermometer placed in position, and a slow stream of oxygen, treated as in the previous determination, passed through the apparatus.

The temperature of the water, if constant, is now noted as the *initial* temperature.

The pellet is now ignited by connecting up the battery (4 volts) for 10 seconds, after which the ignition wire is drawn up near the top of the combustion chamber. The time at which the combustion is started is noted.

The slow stream of oxygen is allowed to pass until combustion is nearly complete, when it is gradually increased in order to ensure total combustion. When the sample is completely burned, the oxygen supply is cut off and water allowed to fill the combustion chamber by raising the ball of the valve and opening the tap at the top of the combustion chamber. The water is then forced out by turning on the oxygen and closing the outlet tap at the top of the chamber, the oxygen being allowed to pass through the apparatus in order to stir effectually the contents of the calorimeter. The thermometer is carefully watched, and the maximum reading

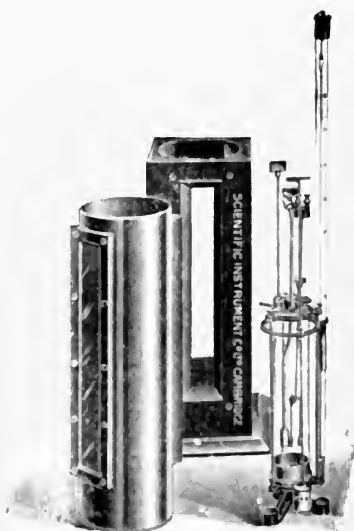


FIG. 44.—Rosenhain calorimeter.

is noted. This will be observed almost immediately after the water is expelled from the combustion chamber.

The time at which the maximum reading is observed is noted, and the whole apparatus is allowed to cool for half the time taken for the combustion. The fall in temperature is added to the observed rise of temperature of the water as the radiation correction.

The water equivalent of the apparatus is determined, as in the case of the William Thomson apparatus, by employing a sample of coal of known calorific value, the ignition wire being heated for the same length of time as in the previous case. The calculation of the calorific power of the coal is exactly the same as described on page 308.

The instrument described above may also be used for determining the calorific powers of oils. In such cases the oil (about 0.5 gram) is absorbed in a weighed pellet of dry compressed cellulose of known calorific value.

If a volatile substance, such as petrol, is employed, the pellet is wrapped in a piece of tinfoil, also of known weight and calorific value. The loss of a certain amount of the lighter constituents of the petrol is inevitable, but this need only be very small. Immediately the pellet is placed in the combustion chamber, a slow stream of oxygen should be passed through the apparatus to prevent the accumulation of explosive vapour, and the combustion should be started as soon as possible.

In the combustion of a liquid fuel in such an apparatus, if the oxygen supply should by any means be cut off during the combustion and the flame become extinguished, no attempt should be made to re-ignite the sample, as, under such conditions, the combustion chamber has probably become filled with an explosive mixture.

For further information regarding the use of this apparatus, see *Journ. Soc. Chem. Ind.*, 1906, page 239.

The Mahler Bomb Calorimeter.—This apparatus is shown in Fig. 45; it is a modification of the original Berthelot bomb calorimeter. The combustion chamber (the bomb), B, is a steel cylinder, 10 cm. external diameter at the lower end, and about 15 cm. high, the walls being about 8 mm. thick. The outer surfaces of the bomb and its cover are nickel-plated, and the inner surfaces covered with enamel to prevent corrosion. In other forms of bomb calorimeters the combustion chamber is lined with gold or platinum.

The cover of the bomb consists of a steel cap which can

be screwed on by means of a special spanner, the bomb meanwhile being fixed in a lead-lined clamp. The joint between the bomb and cover is made gas-tight by means of a lead washer. In other forms of apparatus the cover is fixed on by means of nuts and bolts.

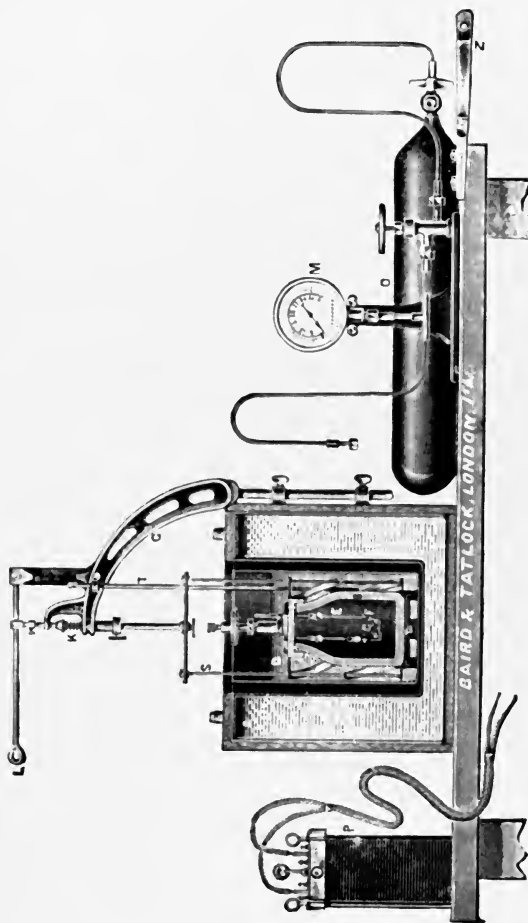


FIG 45.—Mahler bomb calorimeter

A platinum rod, E, passes through the cover, from which it is insulated, and another platinum rod is fixed to the central tube through which the oxygen passes. This rod carries a platinum capsule on which the sample to be tested is placed. The two platinum rods are connected by means of a short,

thin iron wire (about 0.15 mm. diameter) wound round them, and placed in contact with the sample to be burned.

By connecting the insulated rod to one pole of a storage battery of six cells (12 volts), and the cover of the bomb to the other, a current of electricity is passed through the wire, which burns, and from which the combustion is transferred to the sample. The heat produced by the combustion of the iron must, of course, be taken into account in the calculation.

Instead of iron wire, very thin platinum wire (about 0.05 mm. diameter) is sometimes used for the ignition, as if particles of fused iron oxide fall on the enamel of the bomb, this is damaged. With this platinum wire two cells (4 volts) will be sufficient. No correction has to be applied in this case, since the platinum does not burn. In either case, whether iron or platinum be employed, a length of the ignition wire should be tested beforehand, and it should become red-hot on applying the current for one second.

The bomb can be fitted to the copper tube attached to the pressure gauge M, which is connected with the oxygen cylinder.

Oxygen thus passes into the bomb by means of the central tube, which is fitted with a needle-valve operated by means of a screw, the pressure in the bomb being registered by the pressure-gauge. In other forms of apparatus the oxygen is passed into the bomb by means of a side tube, the valve being operated from the top. When charged, the bomb is immersed in a given mass of water in the calorimeter vessel D, and supported in such a manner that free circulation of water round it is possible. The calorimeter vessel is provided with a thermometer T, reading to $\frac{1}{100}$ th of a degree,* and with a stirrer S, worked by means of a lever L, or mechanically by means of a suitable motor.

The calorimeter vessel is surrounded by a water-jacket, and the whole is fitted with a lid, made in two pieces, having holes through which pass the stirrer rods and the thermometer.

In carrying out a determination of the calorific value of a solid or liquid fuel, about 1 gram of the substance (if a solid, preferably in the form of a pellet, otherwise some of the sample may be scattered over the sides of the bomb and escape combustion) is weighed into the platinum capsule

* A Beckmann thermometer, properly adjusted, is quite suitable for this purpose, since it is *rise* of temperature, and not actual temperature, which has to be determined. (See page 316 for method of "setting" the thermometer.)

and the firing wire is adjusted so as to be in contact with the sample.

If iron wire is used for the ignition, a length of about 3 cm. should be wound round a pin, to give it a spiral form, and then weighed, after which it is wound round the platinum rods.

A small quantity of distilled water (about 1 c.c.) is placed in the bomb to dissolve any nitric and sulphuric acids which may be formed, and the cover screwed on, care being taken not to disturb the contents of the capsule.

The bomb is now connected to the pressure gauge and the needle valve partly opened by giving the screw of the valve two complete turns. The valve between the pressure gauge and the oxygen cylinder (pressure gauge valve) is *tightly closed*, after which the valve of the oxygen cylinder may be opened. The valve of the pressure gauge is then opened and oxygen admitted until a pressure of 25 atmospheres is registered, when it is closed, together with the needle valve of the bomb and the valve of the oxygen cylinder.

If the valve of the oxygen cylinder has not been opened sufficiently, it is advisable to close the valve of the pressure gauge before opening the former any further, otherwise the total pressure of the oxygen cylinder may be thrown on the pressure gauge which thereby might be burst. This precaution is not necessary if the gauge is of sufficient range to withstand the pressure of the oxygen cylinder, which, when full, will probably be about 100 atmospheres. In all cases, however, valves should be opened *slowly*.

The bomb is now disconnected from the manometer and placed in the calorimeter vessel, which contains 2500 grams of water weighed to the nearest gram and taken from a supply which has been kept for some time in the room in which the experiment is being carried out. The water-jacket is also filled from the same supply. Before placing the bomb in the calorimeter vessel it is advisable to make sure that it is gas-tight. This can be ascertained by immersing it in water. The bomb must, however, be dried before finally placing it in the calorimeter vessel.

The water in the calorimeter vessel is now stirred until a constant temperature is obtained. One wire from the battery having been attached to the insulated platinum rod which passes through the cover, the stirring is stopped momentarily and the other wire is allowed to touch the cover of the bomb for one second, thereby igniting the sample. With instruments

provided with two terminals for the wires the circuit is completed by inserting the battery key.

The stirring is recommenced and the temperature taken every half-minute for five minutes, or until the maximum temperature is passed, after which it is taken every minute for another five minutes.

The bomb is then removed and the valve opened slowly to relieve the pressure inside, after which the cap is unscrewed and the bomb and cover rinsed out with successive small quantities of water and the washings kept.

In order to complete the calculation it is necessary to know the water equivalent of the calorimeter and the radiation correction.

The water equivalent of the instrument is found by repeating the experiment, using a substance of known calorific power as in the previous cases.

Various systems are in use for calculating the radiation correction. A sufficiently accurate correction is obtained as follows:—

It can be assumed that the rate of loss of heat by radiation is the same before and after the maximum temperature is reached.

With a Mahler calorimeter the maximum temperature will be reached in about three minutes after starting the combustion, and after the maximum is attained the temperature will remain almost constant for a short time, after which it will fall.

The fall in temperature during five minutes after the maximum is passed, divided by five, gives the average rate of loss per minute.

Thus, if the fall in temperature between the fifth and tenth minute after the maximum is passed is 0.08° the rate of fall per minute is $\frac{0.08}{5} = 0.016^\circ$. If the observed maximum, say, 18.64° , was reached in two and a half minutes after starting the combustion, the true maximum temperature may be obtained by adding $0.016 \times 2.5 = 0.04^\circ$ to the observed maximum, or $18.64 + 0.04 = 18.68^\circ$. The true rise in temperature is the true maximum *minus* the initial temperature, say, 16.32° ; or $18.68 - 16.32 = 2.36^\circ$. The calorific value of the substance employed is then calculated as before.

If iron wire was used for the ignition, an amount of heat equal to 1600 calories per gram of iron must be deducted from the total heat produced, so that if 0.004 gram of iron wire is used, the deduction to be made is $1600 \times 0.004 = 6.4$ calories.

In determining the water equivalent of the calorimeter, the heat produced by the combustion of the iron must of course be *added* to that produced by the combustion of the substance of known calorific value in calculating the total heat liberated.

In accurate work it is necessary to make a correction for the amount of nitric and sulphuric acids which are produced.

Any nitrogen which is present in the fuel will, under the conditions of the experiment, be oxidized to nitric acid, and any sulphur to sulphuric acid. Under ordinary conditions of combustion only sulphur dioxide and no nitric acid will be produced.

The amount of acid produced is estimated by titration of the bomb washing with standard sodium carbonate solution.

The heat of formation of nitric acid (in solution) is 230 calories per gram, or 1 caloric corresponds to 0.0044 gram of nitric acid in solution.

From the equation



126 grams of nitric acid are equivalent to 106 grams of sodium carbonate, or 0.0044 gram HNO_3 to 0.003702 gram Na_2CO_3 . So that if the acid solution is titrated with a solution of sodium carbonate containing 0.003702 gram of the pure dry salt per c.c. (or 3.702 grams per litre), the number of c.c. of this solution required for the nitric acid will give the number of calories to be deducted for the formation of this substance.

Some of the total sodium carbonate solution required is neutralized by the sulphuric acid, the amount so used being found by estimating the amount of sulphate in solution after titration, by acidifying and precipitating with barium chloride as on page 165.

The heat of formation of sulphuric acid in solution from sulphur dioxide, oxygen and water being 730 calories per gram, a proportionate amount of heat must be deducted for the amount of sulphuric acid produced.

Since the corrections for the formation of nitric and sulphuric acids do not as a rule amount to more than 0.5 per cent. of the total heat produced, these corrections can often be neglected.

In dealing with a volatile liquid, such as petrol, the liquid should be weighed in a pycnometer tube, and a sufficient quantity blown out on to some kieselguhr placed in the platinum capsule. The cover of the bomb is then immediately

fixed on, after which the pyknometer is again weighed to ascertain the amount of substance taken.

With such a liquid it is advisable to carry out the ignition at a safe distance, as occasionally the thread of the cover has been stripped by the violence of the explosion.

The Beckmann Thermometer.—This thermometer has a range of only 5° or 6° , and is graduated in $\frac{1}{100}$ ths of a degree Centigrade. It is so constructed that the amount of mercury in the bulb can be varied by having a small reservoir of mercury at the upper end of the capillary tube. The thermometer is thus suitable for observing small differences in temperature, as in the cryoscopic or ebullioscopic methods for determining molecular weights, and in accurate calorimetric work.

To "set" the thermometer to read in the neighbourhood of a particular temperature, it is suspended in a beaker of water at a temperature about 2° higher than the highest temperature to be measured in the particular experiment for which the thermometer is required, the temperature of the water in the beaker being taken by an ordinary thermometer.

If the thread of the mercury does not appear on the scale of the Beckmann thermometer under such conditions, the bulb of the thermometer is placed in a beaker of water, which is heated gently until the thread rises to the top and forms a small drop at the end of the capillary. The thermometer is now quickly inverted and tapped gently so as to unite the mercury in the reservoir with that projecting from the capillary.

It is then replaced carefully in the first beaker in the normal position, and after a few minutes, when the bulb and contents have taken the temperature of the bath, the upper end is tapped gently against the palm of the hand, so as to break off the excess of mercury from the end of the capillary.

The thermometer should now be tested to make sure that the thread stands on the scale when the bulb is placed in water at the *highest* and *lowest* temperatures that it will be required to measure in the experiment.

If, on the other hand, the bulb contains too much mercury at the commencement, the excess is shaken off as before, and the thermometer then tested to see if the thread is on the scale.

CHAPTER XXIII

THE RELATIVE VALUES OF PETROL, BENZENE, AND ALCOHOL AS MOTOR FUELS *

THE equations representing the combustion of these three substances (regarding for the moment petrol as consisting solely of the hydrocarbon hexane C_6H_{14}) are as follows:—



From these equations the following data may be obtained:—

	Petrol (Hexane C_6H_{14})	Benzene (pure)	Alcohol (absolute)
Volumes of oxygen required for combustion of one volume of vapour .	9'5	7'5	3
Approximate volume of air corresponding to this volume of oxygen	47'5	37'5	15
Percentage, by volume of vapour in the above mixture with air . . .	2'1	2'6	6'25

* It is not proposed to deal here with the economic aspect of the question. It appears to be recognized on all sides that the need for a petrol substitute will sooner or later become urgent, and for various reasons alcohol seems to be regarded as most suitable for this purpose. For data as to the cost of production of alcohol, exhaustion of petrol supplies, improbability of greatly extended use of benzene as a motor fuel, and further information as to use of alcohol as a fuel, reference should be made to a paper by W. R. Ormandy, *Journal of the Royal Society of Arts*, 1914, Vol. 62, page 234, and discussion thereon, *ibid.*, page 240; V. B. Lewes's "Liquid and Gaseous Fuels" (Constable), chapter on "The Fuel of the Future"; J. S. S. Brame's "Fuel" (Arnold). See also Report of Government Select Committee on Industrial Alcohol: 1905 (Wyman), and Motor Union Fuels Report, 1907; Mersean, *Journ. Soc. Chem. Ind.*, 1914, page 626, this paper also discusses the use of kerosene as a motor fuel.

	Petrol (Hexane C_6H_{14})	Benzene (pure)	Alcohol (absolute)
Litres of oxygen at N.T.P. required for 1 kilogram of fuel.	2474	2154	1461
Cubic feet of air required per gallon,* at 0° C. and 760 mm.	1343	1532 †	932
Calorific power (gross) of 1 kilo- gram, in kilogram-calories	11,520	10,243	7413
Calorific power (gross) of 1 gallon* in British Thermal Units	140,300	163,400	106,100
Ratio of calorific powers per kilo- gram	1	0·89	0·64

It will be seen from the table that the calorific powers per kilogram are in the proportions 1·0, 0·89, 0·64 for hexane, benzene, and alcohol respectively, and it would appear from this consideration alone that alcohol was the least efficient fuel of the three.‡

It has been found, however, that in the petrol and benzene engines a large percentage of the carbon and hydrogen of the fuel is not burned, a consequent diminution of the calorific effect resulting, whilst with alcohol it is easier to get approximately complete combustion.§

In addition to calorific value, another important consideration in connexion with a fuel for an internal combustion engine is the extent to which the explosive mixture of its vapour with air can be compressed without pre-ignition: in general the higher the compression the greater the efficiency.

With petrol and benzene the compression must not exceed 70–80 pounds per square inch, whereas with alcohol the mixture will withstand a compression about three times as great without pre-ignition, and this high compression, which is

* Taking densities : hexane = 0·676, benzene = 0·886, alcohol = 0·794.

† Assuming benzene to remain liquid at 0° C.

‡ For relative calorific powers of petrol, 90 per cent. benzol and methylated spirit, see Brame's "Fuel," page 158.

§ On this account the exhaust gases from an alcohol engine are much freer from objectionable odour than those from a petrol or benzene engine.

possible with alcohol, practically counterbalances its low calorific value.

Another advantage of alcohol over the other two fuels is met with in connexion with what is known as explosive range.

From the data given in the table above, it will be seen that the volumes of air required for the complete combustion of one volume of each of the fuel vapours are 47·5, 37·5 and 15 for petrol, benzene and alcohol respectively.

It is obvious that mixtures of these vapours and air, in proportions other than these, will be explosive, but there is a maximum and a minimum limit for the amount of vapour above and below which the mixture ceases to be explosive. These explosive limits are as follows :—

	Approximate percentage by volume of vapour in air.	Range.
Petrol	1—5	4·0
Benzene	2·7—6·3	3·6
Alcohol	4·0—13·6	9·6

The large range in the case of alcohol is obviously an advantage in preventing misfiring.

A large number of trials have been made with reference to the use of alcohol as a fuel, and, in general, it appears to have been found that the relative efficiencies of engines specially adapted for the particular fuels and running respectively on *benzene*, *petrol*, and *alcohol*, although practically the same, show a slight falling off in the order named.

One drawback to the use of benzene as a motor spirit is the possibility of solidification at low temperatures, since the freezing point of pure benzene is 6° C., but, as explained on page 230, the presence of its higher homologues in benzene tends to lower its freezing point.

In view of the possibility of the use of benzene as a denaturant for alcohol (see page 268) the following figures, taken from the results of the work of Goolich, which was carried out at the Berlin Fermentation Institute, to show the effect of the addition of benzene on the consumption of fuel per horse-power, are of interest.

Benzene percentage by weight.	H.P. developed.	Consumption in grams per H.P.	Percentage. Economy in fuel compared with unmixed alcohol.*
0	8.809	420	—
5	8.862	405	3.6
10	8.888	387.5	8.0
15	8.867	386.5	9.0
20	8.819	370	12.0
25	8.887	386	8.0
30	8.880	390.5	7.0

A mixture of 20 per cent. by weight of benzene and 80 per cent. by weight of the alcohol thus appeared to be most economical. It should be noted, however, that if the percentage of water in the alcohol is high, complete admixture of the benzene does not take place.

Other points in connexion with the use of alcohol may be mentioned.

The low volatility of alcohol [B.P. 78° C., flash point about 17° C. (65° F.)] is obviously a disadvantage in starting a cold engine. The homogeneous character of alcohol as regards volatility is, however, an advantage possessed by this fuel over many varieties of petrol.

It will be seen from the vapour densities of alcohol $\frac{4.6}{2} = 23$ and hexane $\frac{8.6}{2} = 43$, that the vapour of the former is less likely to accumulate on low levels than that of petrol, whilst if such accumulation does take place, as previously pointed out, a larger proportion of alcohol vapour is required to form an explosive mixture with air than is the case with petrol.

A minor objection to alcohol is its high latent heat of vaporization (203) as compared with those of hexane (79.4) and benzene (94.4).

Corrosion with Alcohol.—It was anticipated that the employment of alcohol as a substitute for petrol in internal combustion engines would lead to the rapid destruction of the valves, etc., of the engine owing to the formation of acetic acid and other substances as oxidation products of the alcohol.

Trillat states that the three stages in the oxidation of alcohol take place as follows:—

* The alcohol used contained 86 per cent. by weight of ethyl alcohol.

- (1) $200^{\circ}\text{--}400^{\circ}\text{C. C}_2\text{H}_5\text{OH} + \text{O} \longrightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$
Acetaldehyde.
- (2) $400^{\circ}\text{--}500^{\circ}\text{C. C}_2\text{H}_5\text{OH} + \text{O}_2 \longrightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$
Acetic acid.
- (3) $\text{above } 500^{\circ}\text{C. C}_2\text{H}_5\text{OH} + 3\text{O}_2 \longrightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$

In actual practice, however, no serious difficulty due to this cause seems to be encountered, and the acid products do not appear to attack the metal whilst the engine is hot. It is generally found that the silencer is most attacked, and by employing petrol or benzene for a short time before the engine stops running, the possibility of corrosion from alcohol is entirely removed.

The use of wood spirit as a denaturant for alcohol intended for use as a motor spirit is objectionable, since methyl alcohol gives formaldehyde at a comparatively low temperature, 160°C . This formaldehyde is readily converted into formic acid.

The molecular heat of combustion of methyl alcohol is also only 182 Cal. as compared with 342 Cal. for ethyl alcohol.

The effect of Water in Alcohol intended for Use as a Motor Spirit.—Alcohol and water are miscible in all proportions, and it is difficult to remove the last traces of water from alcohol.

This miscibility of alcohol and water introduces a complication with regard to the use of alcohol as a motor spirit, which is not met with in connexion with petrol or benzene, neither of which is miscible with water.

It has been found that with 80 to 94 per cent. alcohol the consumption of *pure* alcohol is approximately the same, that is, between these limits the total quantity of diluted alcohol employed is almost directly proportional to the amount of water present. There would thus appear to be no necessity to extract the last fraction of the water from alcohol intended for use as a motor spirit, and thus considerable expense is saved.

CHAPTER XXIV

STATISTICS, TYPICAL ANALYSES AND SPECIFICATIONS.

OUTPUT OF PETROLEUM * (in Barrels of 42 American gallons, equal to 35 Imperial gallons).

Brame, "Fuel," p. 367.

Countries.	1909.	1910.	1911.	1912.
United States . .	183,170,874	209,556,048	220,449,391	222,113,218
Russia	65,970,350	70,336,574	66,183,691	68,019,208
Galicia	14,932,709	12,673,868	10,485,726	8,535,174
Dutch East Indies	11,041,852	11,030,620	12,172,949	10,845,624
Roumania . . .	9,327,278	9,722,958	11,101,878	12,991,913
India	6,676,517	6,137,990	6,451,203	7,116,672
Mexico	2,488,742	3,332,807	14,051,643	16,558,215
Japan	1,889,563	1,930,661	1,658,903	1,671,405
Peru	1,316,118	1,330,105	1,368,274	1,751,143
Germany	1,018,837	1,032,522	1,017,045	995,764
Canada	420,755	315,895	291,096	243,614
Italy	42,388	42,388	74,709	86,286
Other countries .	30,000	30,000	200,000	250,000
Totals	298,326,073	327,472,256	345,512,185	351,178,236

COMPARISON OF BOILING POINTS OF PARAFFINS, OLEFINES, AND POLYMETHYLENES.

No. of Carbon atoms.	Paraffins BP.	Olefines BP.	Polymethylene BP.
3	Propane -45° C.	Propylene -48°	Trimethylene -35°
4	<i>n</i> -Butane 0°	<i>n</i> -Butylene -5°	Tetramethylene $+12^{\circ}$
5	<i>n</i> -Pentane 36°	<i>n</i> -Amylene 39°	Pentamethylene 49°
6	<i>n</i> -Hexane 69°	<i>n</i> -Hexylene 68°	Hexamethylene 81°
7	<i>n</i> -Heptane 98°	<i>n</i> -Heptylene 98°	Heptamethylene 117°
8	<i>n</i> -Octane 126°	<i>n</i> -Octylene 124°	Octomethylene 146°
9	<i>n</i> -Nonane 150°	<i>n</i> -Nonylene 153°	Nonomethylene 171°

* By permission. From "Fuel: Solid, Liquid and Gaseous," by J. S. S. Brame. London: Edward Arnold. 12s. 6d. net.

EFFECT OF TEMPERATURE ON THE VISCOSITY OF OILS.*

J. Veitch-Wilson (Allen's "Comcl. Org. Anal." (1911), Vol. III. p. 148.)

Oil.	Number of seconds required for outflow of the oil.		
	At 15.5° C.	At 49° C.	At 82° C.
Sperm	47	30.5	25.75
Olive	92	37.75	28.25
Lard	96	38	28.5
Rape	108	41.25	30
Neat's-foot	112	40.25	29.25
Tallow (oil)	143	37	25
Engine tallow	Solid	41	26.5

COMPARISON OF REPRESENTATIVE CRUDE PETROLEUMS FROM DIFFERENT OIL-FIELDS.†

Source.	Specific gravity.	Distillate by volume.			
		0°-150° C.		150°-300° C.	
		per cent.	sp. gr.	per cent.	sp. gr.
Pennsylvania	0.820	21.0	0.718	41.0	0.798
Ohio (Lima)	0.838	9.7	0.728	37.1	0.787
Illinois (Randolph County)	0.842	14.0	0.729	37.0	0.797
Kansas (Wilson County)	0.835	19.0	0.720	38.1	0.808
Oklahoma (Glenn Pool)	0.846	8.5	0.756	42.0	0.800
West Virginia	0.787	16.5	0.711	41.0	0.769
California (Coalinga)	0.915	5.7	0.771	34.1	0.858
„ (Kern River)	0.961	—	—	20.2	0.862
„ (Los Angeles)	0.971	—	—	26.3	0.885
„ (Whittier Field)	0.929	4.2	0.773	38.3	0.870
Texas	0.910	2.9	0.794	39.8	0.876
Russia (Grozni)	0.869	13.4	0.730	25.6	0.808
Roumania (Bushtenari)	0.842	35.4	0.734	29.8	0.840
„ (Campina)	0.824	37.7	0.729	30.5	0.823
Burma (Yenangyat)	0.840	17.8	—	49.4	—
Italy (Villeia)	0.787	55.0	—	42.0	—
Japan (Echigo)	0.862	21.8	—	38.8	—

* By permission. From Allen's "Commercial Organic Analysis" (J. and A. Churchill).

† By permission. From A. Beeby Thompson's "Petroleum Mining" (Crosby Lockwood & Son).

ANALYSIS OF COAL.*

Clowes and Coleman, "Quantitative Analysis."

	Anthracite.	Non-caking.	Caking.
Moisture	—	11·72	4·36
Volatile matter	6·48	47·34	35·92
Coke	93·16	50·08	57·94
Ash	1·68	2·58	1·78
Sulphur	0·77	0·57	2·11

BROMINE ABSORPTIONS OF OILS.†

Description of substance.	Specific gravity at 60° F.	Grams of bromine reacting with 100 grams of sample.
Scotch shale naphtha	0·734	42·2
{ 1st 10% from fractional distillation of above	0·699	47·4
{ 5th ditto	0·731	41·3
{ 9th ditto	0·753	38·8
Naphtha from Russian petroleum . .	0·730	4·0
Scotch shale burning oils—		
A.	0·804	24·9
B.	0·802	27·2
C.	0·800	23·8
D.	0·802	24·2
Scotch shale lubricating oils—		
A.	0·960	19·6
B.	0·955	18·5
C.	0·908	14·5
American lubricating oils—		
A.	0·905	6·1
B.	0·916	5·0

* By permission. From Clowes and Colman's "Quantitative Analysis" (J. and A. Churchill).

† Taken principally from results of McArthur, *Journ. Soc. Chem. Ind.*, 1888, 66.

ADMIRALTY SPECIFICATION FOR OIL FUEL (1912).

Quality.—The Oil Fuel supplied shall consist of liquid hydrocarbons, and may be either :—

(a) Shale oil ; or

(b) Petroleum as may be required ; or

(c) A distillate or a residual product of petroleum,

and shall comply with the Admiralty requirements as regards flash point, fluidity at low temperatures, percentage of sulphur, presence of water, acidity, and freedom from impurities.

The flash point shall not be lower than 175° F., closed test (Abel or Pensky-Martens).*

The proportion of sulphur contained in the oil shall not exceed 3'00 per cent.

The oil fuel supplied shall be as free as possible from acid, and in any case the quantity of acid must not exceed 0'05 per cent. calculated as oleic acid when tested by shaking up the oil with distilled water, and determining by titration with decinormal alkali the amount of acid extracted by the water, methyl orange being used as indicator.

The quantity of water delivered with the oil shall not exceed 0'5 per cent.

The viscosity of the oil supplied shall not exceed 2000 seconds for an outflow of 50 cubic centimetres at a temperature of 32° F., as determined by Sir Boverton Redwood's "Standard Viscometer" (Admiralty type for testing oil fuel).

The oil supplied shall be free from earthy, carbonaceous, or fibrous matter, or other impurities which are likely to choke the burners.

The oil shall, if required by the Inspecting Officer, be strained by being pumped or discharged from the tanks, or tank steamer, through filters of wire gauze having 16 meshes to the inch.

The quality and kind of oil supplied shall be fully described. The original source from which the oil has been obtained shall be stated in detail, as well as the treatment to which it has been subjected, and the place at which it has been treated.

The ratio which the oil supplied bears to the original crude oil should also be stated as a percentage.

* In the case of oils of exceptionally low viscosity such as distillates from shale, the flash point must be not less than 290° F.

TYPICAL SPECIFICATION FOR OIL USED FOR "CRACKING"
FOR GAS.

1. Specific gravity 0·845 to 0·865 at 60° F.
2. Flash point—not lower than 73° F., by Abel closed test and as far as possible not lower than 120° F.
3. Solid residue on evaporation to dryness not to exceed 1 per cent.

Results of Examination of a Sample supplied to this Specification.

Colour, greenish-brown.

Specific gravity 60° F. 0·861.

Flash point 123° F. (50·5° C.).

Distillation.

First drop 160° C.

	Per cent.	Colour.
160°–240°	7·3	Greenish-yellow.
260°	1·5	Straw.
280°	4·4	Paler.
290°	4·0	"
300°	4·1	Green.
310°	7·4	"
320°	6·0	"
330°	8·9	"
340°	7·1	Deep straw.
350°	9·1	"
360°	9·5	Greenish.
370°	6·7	Gold brown.
380°	14·0 }	Viscous.
390°	1·5 }	
Above and loss . .	8·5	
	100·0	

Residue on complete distillation 0·7 per cent.

Result of "Cracking" One Gallon of this Oil.

Retort temp. (average).	Yield.	Illuminating power.	Multiple. (Yield × Ill. Power).
1535° F.	80·3 c. ft.	39·6 candles.	3180
1470° F.	69·4 "	46·9 "	3250

YIELD OF ALCOHOL PER TON OF VARIOUS SUBSTANCES.

E. A. Mann, *Journ. Soc. Chem. Ind.*, 1906, 1076.

	Proof gallons per bushel of 60 lbs.	Equal to a yield in gallons per ton.	
		Absolute alcohol.	90 per cent. alcohol.
Pure starch	4.68	82.0	95.0
Wheat, barley, oats, etc. (average)	2.08	38.0	42.0
Potatoes (21 per cent. starch) . .	1.26	23.5	25.5
Sugar cane (12 per cent. sugar) . .	0.72	13.5	14.7
Beet (10 per cent. sugar)	0.60	11.25	12.25

MOLECULAR HEATS OF COMBUSTION (GROSS) IN KILOGRAM CALORIES.

Name.	Formula.	Cals.
Methane	CH_4	212
Ethane	C_2H_6	370
Propane	C_3H_8	529
Iso-butane	C_4H_{10}	687
Ethylene	C_2H_4	341
Propylene	C_3H_6	492
Iso-butylene	C_4H_8	650
Iso-amylene	C_5H_{10}	807
Acetylene	C_2H_2	314
Allylene	C_3H_4	468
Pentamethylene	C_5H_{10}	790
Hexamethylene	C_6H_{12}	933
Heptamethylene	C_7H_{14}	1099
Benzene	C_6H_6	799
Toluene	C_7H_8	933
Methyl alcohol	CH_3OH	182
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	342

CALORIFIC POWERS (GROSS) OF COALS.*

Brame, "Fuel," p. 68.

	Kilogram calories per kilogram.	B. Th. U. per pound.
Splint coals	7700-8150	13,850-14,650
Bituminous	8000-8700	14,600-15,300
Coking	8300-8600	14,940-15,480
Smokeless Steam . .	8700-8900	15,650-16,000
Anthracite	8700-8800	15,650-15,800

CALORIFIC POWERS (GROSS) OF PETROLS.

B. Blount, *Inst. Automobile Engs.*, March, 1909, pp. 1-6.

Trade Description.	Specific gravity.	Kilogram Calories per kilo.	B. Th. U. per lb.	B. Th. U. per gallon.
Anglo 0.760	0.739	11,162	20,092	148,480
Shell	0.717	11,252	20,254	145,220
Pratt's	0.717	11,229	20,212	144,920
Carless Capel "Standard" .	0.700	11,302	20,344	142,400
" " "Movril" .	0.718	11,200	20,160	144,760
Carburine	0.717	11,187	20,137	144,380
Russian	0.705	11,232	20,218	142,530

NET CALORIFIC POWERS OF PETROLS.

W. Watson, *Journ. Royal Soc. Arts*, 1910, 58, 990.

Petrol.	Density.	Kilogram Calories per kilo.	B. Th. U. per lb.	B. Th. U. per gallon.
Bowley's special	0.684	10,660	19,190	131,500
Carless	0.704	10,420	18,760	132,300
Express	0.707	10,020	18,040	127,600
Ross	0.714	10,370	18,670	133,600
Pratt	0.719	10,340	18,610	134,100
Carburine	0.720	10,380	18,680	135,000
Shell	0.721	10,400	18,720	135,300
Dynol	0.725	10,290	18,520	134,600
Sun car benzol	0.762	9,490	17,080	130,400
0.760 Shell (Crown) . .	0.767	10,140	18,250	140,300

* By permission. From "Fuel: Solid, Liquid and Gaseous," by J. S. S. Brame. London: Edward Arnold. 12s. 6d. net.

COMPOSITION AND CALORIFIC POWER OF PARAFFIN OILS.

W. Inchley, *The Eng.*, 1911, 111, 155.

Name.	Specific gravity.	Composition.				Calorific power.	
		Carbon.	Hydrogen.	Oxygen, Nitrogen, etc.	Kilogram Calories per kilo.	B. Th. U. per lb.	B. Th. U. per gall.
Royal Daylight (American)	0.797	85.70	14.20	—	11,167	20,100	159,000
Kerosene (American)	0.780	85.05	14.40	0.55	11,163	20,095	156,500
Refined (Baku)	0.825	86.00	14.00	—	11,270	20,300	167,000
Russol, R.U.O.	0.890	85.95	13.50	0.45	10,901	19,620	174,500
Solar Oil . . .	0.896	86.61	12.60	0.79	10,783	19,450	174,000

CALORIFIC POWER AND SPECIFIC HEAT OF PARAFFIN OILS (BRAME).*

Brame, "Fuel," page 170.

Name.	Specific gravity.	Calorific power.				Specific heat.
		Kilogram Calories per kilo.	B. Th. U. per pound.	B. Th. U. per gall.		
Royal Daylight (Tea Rose)	0.8055	11,100	19,980	160,500		0.450
Water White (White Rose)	0.800	11,140	20,050	160,400		0.457
Russian	0.8248	11,060	19,910	164,000		0.435
Roumanian . . .	0.8127	10,900	19,620	159,500		0.444

RELATION BETWEEN SPECIFIC GRAVITY AND CALORIFIC POWER.

Sherman & Kropff (*Jour. Amer. Chem. Soc.*, 1908, 30, 1626).

The following formula has been found to express approximately the relation between the specific gravity and the calorific power (in British thermal units per pound) of American petroleum oils.

$$\text{B.T.U.} = 18,650 + 40 (\text{Baumé degrees} - 10).$$

* By permission. From "Fuel: Solid, Liquid and Gaseous," by J. S. S. Brame. London: Edward Arnold. 12s. 6d. net.

The relation between calorific power and specific gravity for similar oils is also indicated below, the calorific powers being expressed in calories per gram.

Specific gravity.	Calorific power. *
0.70-0.75	11,700-11,350 calories
0.75-0.80	11,350-11,100 ,,
0.80-0.85	11,100-10,875 ,,
0.85-0.90	10,875-10,678 ,,
0.90-0.95	10,675-10,500 ,,

CHAPTER XXV

RELATION OF METRIC AND ENGLISH UNITS

1 metre	= 39.37 inches
1 inch	= 2.54 centimetres
1 cubic inch	= 16.386 c.c.
1 cubic foot	= 28.32 litres
1 fluid ounce	= 28.39 c.c.
1 gallon	= 4.546 litres
1 litre	= 35.22 fluid ounces
1 grain	= 0.0648 grams
1 gram	= 15.43 grains
1 pound (avoirdupois)	= 453.6 grams
1 kilogram	= 2.205 pounds (avoirdupois)
1000 kilograms (1 metric ton)	= 0.9842 tons
1 ton	= 1016 kilograms
1 Cal. (kilogram degree Centigrade)	} = { 3.96 B.T.U. (pound degree Fahrenheit)
Calorific power of 1 Cal. per kilogram	
	} = { 1.8 B.T.U. per pound. (See page 299.)

QUESTIONS AND NUMERICAL EXAMPLES.

CHAP I.—I. What alterations in properties are usually found to occur among the members of a homologous series of hydrocarbons as the molecular weight increases?

2. Construct graphic formulæ for all the theoretically possible (a) hexanes, C_6H_{14} , (b) amyl alcohols, $C_5H_{11}OH$.

3. What are the principal differences in properties between aliphatic and aromatic hydrocarbons?

4. Give examples of the conversion of compounds belonging to the aliphatic series into derivatives of benzene.

5. How may methane be converted into methylamine, nitromethane, methyl alcohol, formic acid, methyl chloride?

6. How may acetylene be prepared? What happens when this gas is (i) passed through a red hot tube?

(ii) mixed with nitrogen and submitted to the action of electric sparks?

(iii) bubbled into silver nitrate and into ammoniacal cuprous chloride solutions?

(iv) treated with chlorine?

7. What reactions are typical of compounds containing

(i) the Carbonyl group?

(ii) the Hydroxyl group?

(iii) the Amino group?

(iv) the Nitro group?

(v) the Amide group ($-\overset{\overset{O}{\parallel}}{C}-NH_2$)?

8. How may the principal members of the polymethylene or naphthene series containing from three to eight carbon atoms in the molecule be prepared?

What alterations in physical and chemical properties are observed as the number of carbon atoms in the ring increases?

How may benzene derivatives be converted into derivatives of

(a) Cyclohexane, (b) Cyclopentane?

9. What are the most characteristic chemical properties exhibited by substances containing the linkage $\text{>C}=\text{C}<$?

Compare these properties with those associated with the linkage $-\text{C}\equiv\text{C}-$. Do all hydrocarbons containing this last-named group exhibit similar properties? If not, what is the reason for the divergence?

10. What is an ester? How may it be prepared from an alcohol and how may the alcohol subsequently be regenerated? Why is it that quantitative yields of esters are difficult to obtain? How may the yield be increased?

11. To what classes of compounds do the following substances belong:—

Soap, marsh gas, acetylene, olive oil, chloroform, cane sugar, starch, butter?

Mention any notable reactions which each may be caused to undergo, giving equations.

12. Mention the reactions which tend to show that the substituents in a benzene nucleus are "firmly fixed" and that the substituents in *e.g.* a substituted ethane are comparatively loosely bound.

13. What are phenols? What is the principal source of these compounds? How may they be prepared? In what respect do they differ from aliphatic alcohols?

14. Describe carefully the properties of the various substances which can be obtained by the interaction of sulphuric acid and ethyl alcohol. What special conditions are necessary to the formation of each of these compounds? Explain the mechanism of the actions in which they are formed.

15. By what tests would you distinguish hexane, hexamethylene and benzene?

16. Give an account of the methods you would employ for the conversion of

(a) Benzoic acid into aniline.

(b) Benzoic acid into benzamide.

(c) Benzamide into benzoic acid.

(d) Benzene into benzenesulphonic acid and the latter into phenol.

17. Starting from ethyl alcohol, describe how you would synthesize

(a) Ethyl sulphuric acid.

(b) Ethyl bromide.

(c) Ethyl cyanide.

(d) Diethyl ether.

(e) Ethylene.

18. Give an account of the preparation and properties of paraldehyde and aldol and state how the accepted formulæ account for the differing stabilities of these substances.

19. Illustrate clearly by as many examples as possible the applications of the terms

Addition, Substitution, Reduction, Hydrogenation, Sulphonation, Esterification, Saponification.

20. On what grounds is the formula $\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{CHO}$ assigned to glucose? What other formula has been put forward recently?

How may glucose be obtained from (a) Starch, (b) Wood, (c) Cane sugar?

21. The product of the action of methyl iodide on silver nitrite consists of a mixture of two substances. How may these be separated? What are their properties and constitutional formulæ, and on what evidence are these formulæ based?

22. What are primary, secondary and tertiary alcohols and amines? How may they be distinguished from each other? What is a tertiary carbon atom?

23. An ester has the molecular formulæ $C_5H_{10}O_2$. What are the possible structural formulæ for this substance? How could one distinguish between the various substances possessing this composition?

24. Assuming potatoes to contain 21% by weight of starch, what weight of absolute alcohol is theoretically obtainable from one ton of potatoes? (*Ans.* 0.12 ton.)

25. Benzene and other aromatic hydrocarbons react with sulphuric acid producing compounds having acidic properties; so also do ethylene and its homologues. What are the differences in properties and constitution between the two types of acids which are produced?

CHAPS. IV. and VII.—1. What volume of methane could theoretically be obtained from (a) 1 kilogram of anhydrous sodium acetate by the action of soda lime; (b) by the decomposition of 1 kilogram of aluminium carbide which contains 80 per cent. Al_4C_3 ?

The gas is to be measured in both cases at 10° C. and 750 mm. pressure. [$C = 12$, $Na = 23$, $O = 16$, $Al = 27$.]
(*Ans.* (a) 287 litres; (b) 392.1 litres.)

2. What volume of chlorine is required to convert 1 litre of marsh gas into methyl chloride, and what volume of methyl chloride is produced, all the gases being measured at 20° C. and 740 mm. pressure?
(*Ans.* 1 litre Cl_2 and 1 litre of CH_3Cl .)

3. What weight of bromine is required for the complete saturation of 1000 litres of ethylene, the gas being measured at 15° C. and 750 mm. pressure? [$Br = 80$.]
(*Ans.* 668.2 grams.)

4. What weight of cuprous acetylide could be produced from 1000 litres of acetylene at 10° C. and 740 mm.? [$Cu = 63$.]
(*Ans.* 629.0 grams.)

5. 5 c.c. of a gaseous hydrocarbon mixed with 20 c.c. of oxygen gave on explosion 15 c.c. of gas, of which 10 c.c. were absorbed by potassium hydroxide solution, and the remaining 5 c.c. by alkaline pyrogallol.

What is the molecular formula of the hydrocarbon? (*Ans.* C_2H_4 .)

6. 10 c.c. of a gaseous hydrocarbon mixed with 30 c.c. of oxygen gave on explosion 25 c.c. of gas, of which 20 c.c. were absorbed by potassium hydroxide, and the remaining 5 c.c. by alkaline pyrogallol.

What is the molecular formula of the hydrocarbon? (*Ans.* C_2H_2 .)

MISCELLANEOUS.

1. How could you detect the presence of benzene in a mixture of this substance with paraffin hydrocarbons?

2. How would you propose to separate a mixture of paraffin, olefine, aromatic, and naphthene hydrocarbons?

3. How could you tell whether a given sample of burning oil were of American or Russian origin?

4. What differences would you expect to find between a crude Russian oil and a crude shale oil?

5. How would you test for the presence of a mineral oil in a sample of a supposed vegetable or animal oil?

6. A specimen of a vegetable oil is found to have a saponification value of 150 instead of 170: what percentage of unsaponifiable matter does the oil contain? (*Ans.* 11.7 per cent.)

7. A sample of olive oil which is supposed to be adulterated with cotton-seed oil gives an iodine value of 90. Taking the iodine values of olive oil and cotton-seed oil as 83 and 107 respectively, what is the percentage of cotton-seed oil in the mixture? (*Ans.* 29.2 per cent.)

8. Calculate the amount of heat theoretically obtainable by the combustion of 1 kilogram and 1 pound of dried coal, which on analysis was found to contain—

Carbon = 85 per cent., hydrogen 5 per cent., oxygen 3 per cent., nitrogen 1 per cent., ash 6 per cent.

Express the results in Kilogram-Calories and B.T.U. respectively.

(*Ans.* (1) 8480 Cals.; (2) 15264 B.T.U.)

9. Calculate the amount of heat theoretically obtainable by the combustion of 1 cubic metre and of 1 cubic foot at N.T.P. of a gas which on analysis is found to contain—

CH_4 = 80 per cent. and C_2H_4 = 20 per cent. (by volume).

Express the result in Kilogram-Calories and B.T.U. respectively.

(*Ans.* (1) 10615 Cal.; (2) 1484 B.T.U.)

10. The ammoniacal liquor and gas washings obtained in the distillation of 1 kilogram of shale are diluted to 1 litre.

50 c.c. of this solution on boiling with excess of sodium hydroxide gave ammonia which neutralized 16.2 c.c. of $\text{N}/2 \text{H}_2\text{SO}_4$.

Calculate the weight of ammonium sulphate in pounds obtainable from 1 ton of the shale. (*Ans.* 24 pounds.)

11. What advantages do the newer vertical gas retorts possess over the older horizontal and inclined retorts?

What is metallurgical coke, how is it produced, and what happens to the bye-products formed simultaneously?

12. What effect has the temperature at which the coal is distilled on—

(i) The composition of the gas?

(ii) The calorific power of the gas?

(iii) The illuminating power of the gas?

What experiments have recently been made on the distillation of coal in a vacuum? Summarize the results which have been obtained.

13. What modifications of the original processes in the distillation, both of shale and of coal, have led to an increased yield of ammonia?

14. Sulphuric acid and caustic soda are used in the refining of crude petroleum, shale, and coal tar oils. On what does the advantageous action of these reagents depend? What other substances are sometimes employed?

15. In what respects do the low-boiling fractions (motor spirits) obtainable from Pennsylvanian petroleum, Caucasian petroleum, shale oil, coal tar, differ from each other?

Which of these fractions would most readily take up hydrogen, and which would be most readily oxidized?

16. A specimen of motor spirit was found to boil from about 80° to 130° , to be perfectly stable towards cold dilute potassium permanganate, and to be only very slowly attacked by cold concentrated sulphuric acid. In fuming sulphuric acid it dissolved immediately.

Concentrated nitric and sulphuric acids produced a yellow oil with an odour of almonds.

When shaken with hydrogen in presence of water and a colloidal palladium solution no absorption took place.

What is the nature of the substances contained in the motor spirit? How might a separation of the constituents be effected?

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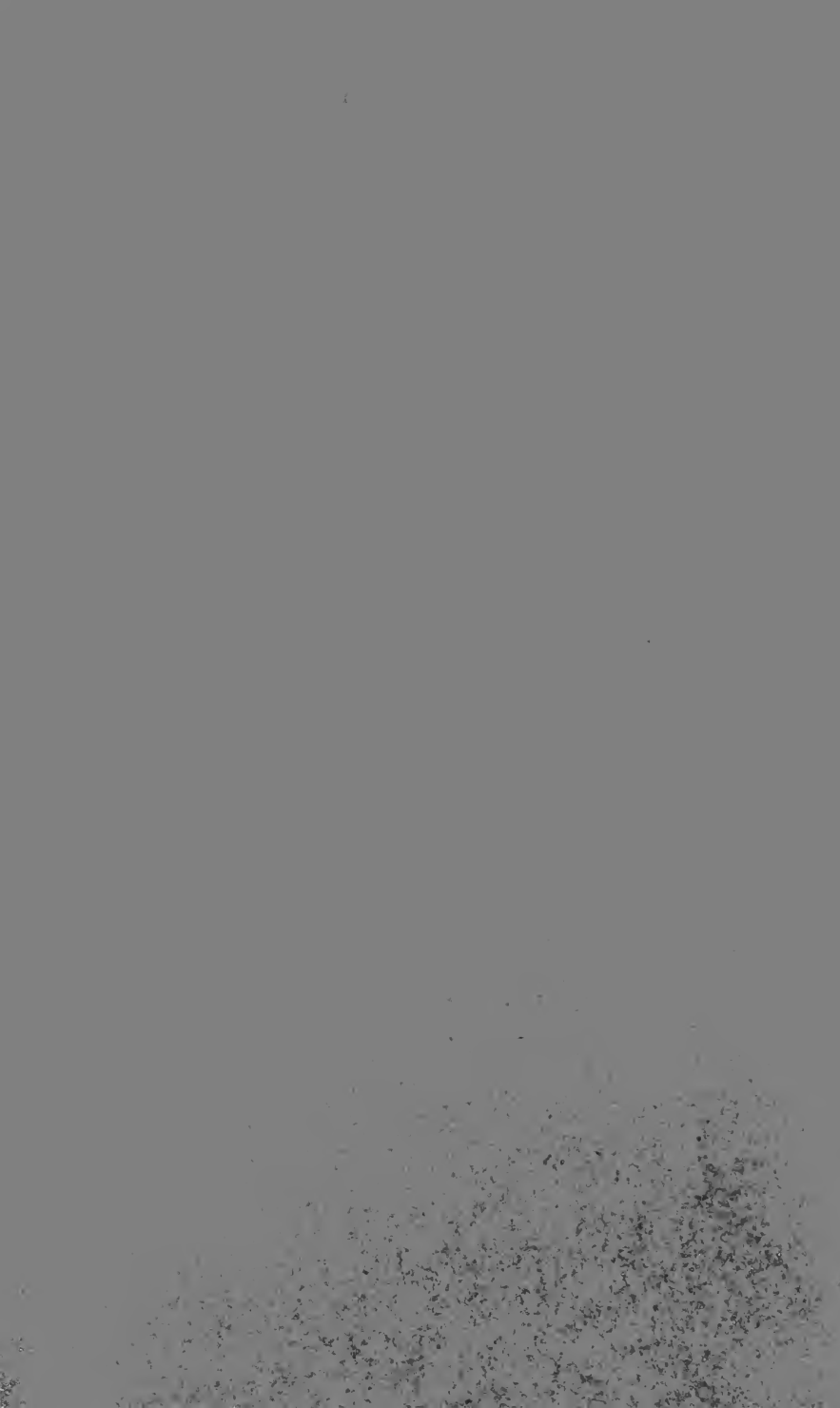
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